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Investigating the effect of Cu/zeolite on deoxygenation of bio-oil from pyrolysis of pine wood

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Abstract

Pyrolysis is one of the significant technologies that can utilize lignocellulose biomass to produce different bioenergy fuels, such as bio-oil, pyrolytic gases and bio-char. The application of pyrolysis has been extensively studied to produce bio-oil, which is foreseen as the potential transportation fuel in the near future. However, the presence of oxygenated compounds, such as phenols and alcohols in bio-oil makes it highly acidic and unstable for a suitable transportation fuel. These oxygenated compounds can be converted to refinable hydrocarbons by using different catalysts. Therefore, this study aimed to prepare a catalyst that is Cu10%-zeolite and investigated its deoxygenation activity for bio-oil produced from pyrolysis of pine wood sawdust. The catalyst was prepared by a wet-impregnation method. Subsequently, the catalyst was characterized by X-ray diffraction and transmission electron microscopy. Furthermore, the catalyst was applied for *in-situ* (catalyst: biomass=5) and *ex-situ* catalytic pyrolysis (catalyst: biomass=3) and the results were compared with those from sole zeolite support. The pyrolysis process was carried out at a heating rate of 100 °C/min to a final temperature of 700 °C and the composition of bio-oil was examined by gas chromatography-mass spectroscopy. The results revealed that Cu-zeolite showed significant deoxygenation activity for bio-oil as compared to zeolite or without any catalyst. Evidently, Cu-zeolite after *in-situ* pyrolysis produced bio-oil with 20.9% aromatic hydrocarbons and 7.5% aliphatic hydrocarbons, which were approximately 80% and several times higher than with only zeolite, respectively. Meanwhile the concentration of alcohols was reduced from 47.5% to 5%. On the other hand, bio-oil produced from *ex-situ* catalytic pyrolysis was enriched with 41.6% aromatic hydrocarbons while only 1% alcohols were present in bio-oil. This promising deoxygenation activity can be ascribed to Cu-zeolite's catalytic activity that converted phenol and alcohols to refinable hydrocarbons via various reactions, such as dehydration, decarboxylation and decarbonylation.

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1. Introduction

Lignocellulose biomass is regarded as a promising and abundant feedstock to produce green and sustainable energy fuels, which have potential to replace the depleting conventional fossil fuels [1, 2]. Pyrolysis is one of the significant technologies that can utilize various types of lignocellulose biomass to produce different bioenergy fuels, such as bio-oil, pyrolytic gases and bio-char [3, 4]. The application of pyrolysis has been extensively studied to produce bio-oil, which is foreseen as the potential transportation fuel in the near future. However, the presence of oxygenated compounds, such as phenols and alcohols in bio-oil makes it highly acidic and unstable for a suitable transportation fuel. These oxygenated compounds can be converted to refinable hydrocarbons by using different homogeneous or heterogeneous catalysts [5]. Zeolites and metal-zeolites have been widely applied for catalytic biomass pyrolysis that have shown promising deoxygenating activity for bio-oil because they are highly acidic in nature and exhibit competitive shape-selectivity properties due to micro/meso pore sizes [6]. Zeolite-based catalysts usually deoxygenate the biomass components via dehydration, decarbonylation and decarboxylation reactions [7]. These catalysts not only decrease the quantity of oxygenated compounds in the bio-oil but also increase the amount of hydrocarbons (aliphatic and aromatic), therefore, upgrading the carbon content in bio-oil and making it more efficient to use as a transportation fuel.

The deoxygenation activity of zeolite catalysts can be further enhanced with the addition of highly catalytically active metals. There are numerous successful studies which showed that the addition of a metal (mainly transition metals) onto a zeolite support significantly improved the deoxygenation activity of the catalyst [7, 8]. For example, Iliopoulou et al. [7] utilized different compositions of Ni/ZSM-5 to upgrade bio-oil from pyrolysis of beech wood. The results showed that ZSM-5 catalyst produced aromatic hydrocarbons in lower concentrations but phenols with comparatively higher concentrations. However, the addition of Ni 10% substantially increased the quantity of desirable aromatic hydrocarbons while the concentration of undesirable acids was considerably reduced in bio-oil [7]. This increase in aromatic hydrocarbons and simultaneous decrease in acids was attributed to improved dehydrogenation pathway on the surface of Ni and ZSM-5. Similarly, in another major study, ZSM-5 was modified with 15% of Fe and was applied for fast pyrolysis of wood sawdust at different temperatures, ranging from 500-800 °C [8]. The results revealed that Fe/ZSM-5 showed better deoxygenation activity and higher production of monocyclic aromatic hydrocarbons as compared to ZSM-5. Besides, it was also noticed that the yield of aromatic hydrocarbons slightly enhanced with increase in temperature. In addition, Fe/ZSM-5 also improved the stability of the catalyst by reducing coke formation on its surface, thereby maintaining the catalytic activity of the catalyst for a longer time.

It is quite evident from previous studies that the addition of metals in zeolite catalyst extensively improves its deoxygenation activity and upgrades the quantity of hydrocarbons in bio-oil composition. Therefore, this study aimed to prepare a Cu10%-zeolite catalyst and investigated its deoxygenation activity for bio-oil produced from pyrolysis of pine wood sawdust. The catalyst was prepared by a wet-impregnation method and was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The *in-situ* and *ex-situ* catalytic pyrolysis processes were carried out at a heating rate of 100 °C/min to a final temperature of 700 °C and the composition of bio-oil samples was examined by gas chromatography-mass spectroscopy (GC-MS). The addition of Cu in zeolite was expected to enhance its deoxygenation activity and increase the formation of desirable hydrocarbons in bio-oil composition.

2. Experimental methodology

2.1. Synthesis and characterization of Cu-zeolite

Cu 10%/zeolite was prepared by a wet-impregnation method. In a typical method, for 10 g of catalyst preparation, required amount of metal precursor $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 50 ml Milli Q water. The required amount of zeolite (Silica-25% alumina with 0.35% Na_2O , Saint Gobain, France) previously calcined at 550 °C for 2.5 h was then added and stirred for 24 h. The resultant solution was heated at 80 °C until the water was completely evaporated, subsequently, dried in a vacuum oven at 110 °C for an overnight. Furthermore, the material was calcined

at 550 °C for 5.5 h. As a result, a green colour powder was obtained as the final product/catalyst. The concentration of Cu in the catalyst was estimated by X-ray fluorescence (XRF), Olympus Delta Pro spectrometer using Ta tube (50 kV). The XRF results confirmed that 10.27% Cu was present in the catalyst, which was close to the estimated concentration of Cu in zeolite.

The crystalline phases of above prepared catalyst were identified by XRD (PANalytical, Netherlands). The XRD patterns were acquired on PANalytical X'Pert Pro MPD X-ray diffractometer by employing CuK α radiations ($\lambda = 1.54056 \text{ \AA}$) and Ni-filter by measuring the X-ray intensity over a diffraction 2θ angle from 5 to 90. The crystallite size of the metal was calculated using the following Scherrer equation:

$$d_{\text{crystallite size}} (nm) = \frac{0.94\lambda}{B \times \cos \theta} \quad (1)$$

where B is full-width at half-maximum (FWHM) of the most intense peak in the spectrum. The morphology of the catalyst was examined using TEM (Philips CM10, Netherlands).

2.2. Pyrolysis operation

Radiata Pine sawdust was used as the biomass in experiments for bio-oil extraction. The furnace used in the study was an infrared image gold furnace (SINKU-RIKO). 0.2 g of biomass was loaded in an inner silica reactor tube. Different catalyst to biomass ratios were used for *in-situ* and *ex-situ* pyrolysis experiments. A catalyst to biomass ratio of 5 was applied for *in-situ* pyrolysis and a ratio of 3 was used for *ex-situ* pyrolysis. The pyrolysis process was carried out at a heating rate of 100 °C/min to a final temperature of 700 °C, using helium as the carrier gas at a flow rate of 50 ml/min. The bio-oil was collected at room temperature by condensing the pyrolytic organic vapours on quartz wool filled at the tube end. Subsequently, the bio-oil was then dissolved in dichloromethane (DCM) solvent and filtered through glass wool and sodium sulfate three times each. The solution was analyzed by a GC-MS system (GC model: Agilent 7890A gas chromatographer with a 60 m HP-5MS column; MS model: 5977A mass spectrometer).

3. Results and discussion

3.1. Catalyst characterization

The prepared catalyst was firstly analyzed by XRD technique to confirm the presence of Cu in zeolite and its crystallinity. Fig. 1 shows the XRD diffraction pattern of Cu-zeolite and zeolite catalysts. It can be analyzed from the results that zeolite was not present in a highly pure crystalline form as only few sharp peaks were observed in the pattern. However, the peaks at 2θ of 39.7°, 46.1°, 66.7°, and 85.06° can be attributed to crystalline zeolite, which are consistent with the standard values of zeolite, ICDD reference code 98-009-3736. On the other hand, Cu-zeolite showed diffraction peaks at 2θ of 35.1°, 39.3°, 48.7°, 53.44°, 58.3°, 61.4°, and 75.2° which can be indexed to (002), (200), (202), (020), (-113), (-311), and (-222) planes of CuO, respectively. These results are well consistent with the standard values of CuO, ICDD reference code 00-045-0937. The determined crystallite size of CuO was 30.58 nm, belonging to the space group of C2/c-15 that indicates the monoclinic structure of the crystals. The morphology of Cu-zeolite was further examined using TEM. Fig. 2 shows TEM images of zeolite (a) and Cu-zeolite (b). The considerable interferences or morphological changes in zeolite particles can be clearly observed in Cu-zeolite when compared to sole zeolite, demonstrating the successful introduction of CuO in zeolite support, as also confirmed by the XRD results.

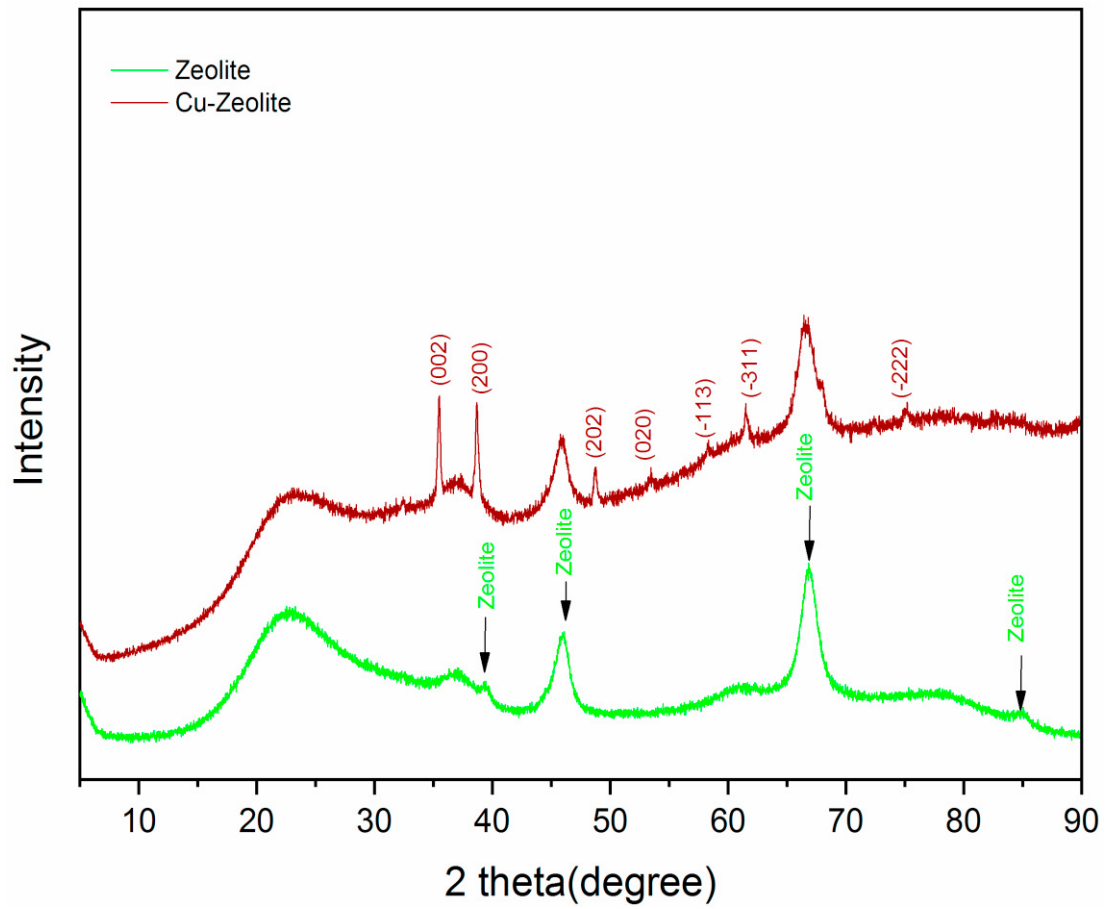


Fig. 1. XRD pattern of Cu-zeolite and zeolite.

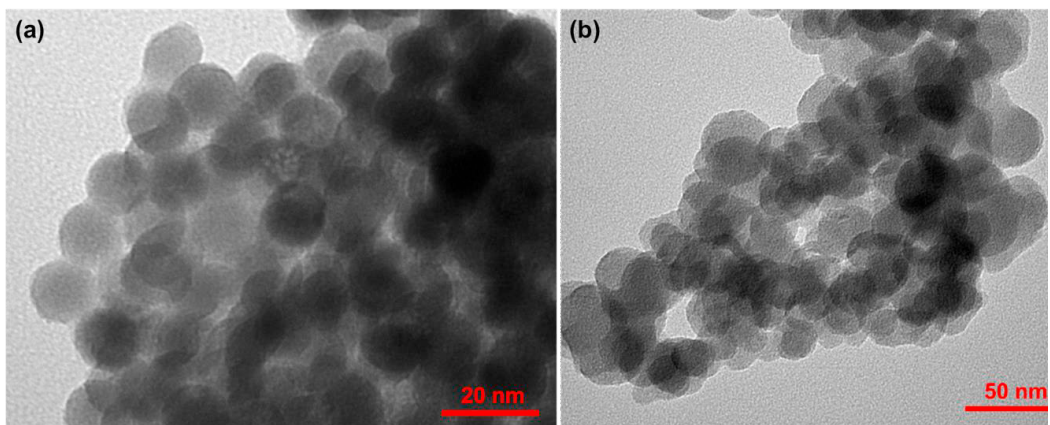


Fig. 2. TEM images of (a) zeolite and (b) Cu-zeolite.

3.2. Bio-oil composition with non-catalytic pyrolysis

After successful identification and characterization of Cu-zeolite, it was applied for *in-situ* and *ex-situ* pyrolysis of pine wood sawdust at 700 °C and the bio-oil samples were analyzed by GC-MS. Forty compounds with the largest peak areas in each GC-MS spectrum were selected for the analysis and were further classified in major eight groups namely aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, acids, nitrogenous compounds (amines, amides and nitriles), furans, aldehydes, ketones and the remaining compounds were designated as others that mainly contained halo alkanes, thio and silicon containing compounds. Fig. 3 represents the bio-oil composition from *in-situ* (a) and *ex-situ* (b) catalytic pyrolysis with and without Cu-zeolite. It can be observed that non-catalytic pyrolysis produced bio-oil with the highest concentrations of alcohols that is 47.53% and produced the least number of hydrocarbons (0.79%) as compared to Cu-zeolite and zeolite. The major oxygenated compounds formed during non-catalytic pyrolysis were different types of phenols, such as phenol, 2-methoxy phenol (5.21%), 2-methoxy-5-methylphenol (9.03%), 2-methoxy-4-vinylphenol (5.97%) and other alcohols like catechol (0.46%) and eugenol (2.92%). The concentration of other undesirable oxygenated compounds i.e. fatty acids in the bio-oil was 5.11%, mainly containing oleic acid (1.17%), dehydroabietic acid (1.17%) and dodecenoic acid (0.84%). In addition, the bio-oil was enriched with nitrogenous compounds, such as pyridine-3-carbonitrile (1.92%), 1-(3, 3, 3-trifluoro-2-hydroxypropyl) piperidine (1.82%), oxazolidine (1.59%) and ketones like 2-cyclopenten-1-one, 3-hydroxy-2-methyl (1.83%), 2-propanone, 1-(4-hydroxy-3-methoxyphenyl) (2.3%), levoglucosenone and only aldehyde that is vanillin was present (2.18%) in the bio-oil. The merely hydrocarbon formed during non-catalytic pyrolysis was stigmasta-3, 5-diene, contributing just 0.79% of the total bio-oil composition.

The composition of bio-oil from pyrolysis of pine wood sawdust obtained in this study was consistent with the previous studies [9-11] that produced almost similar types of compounds using pine wood sawdust as the feedstock. Pine wood is mainly composed of cellulose, hemicellulose and lignin. Generally, cellulose decomposes at 315-400 °C via two pathways, either through depolymerisation to form anhydro-sugars or by ring scission reaction to form light compounds, such as acetic acid, methanol, propionic acid and acetone [12]. Firstly, levoglucosan is formed from cellulose pyrolysis which further breaks down to various light oxygenates by ring scission reaction as mentioned earlier [12]. Hemicellulose decomposes at 220-315 °C and its thermal pyrolysis generates light oxygenates almost similar to cellulose pyrolysis [12, 13]. However, in the current experiments, bio-oil was highly enriched with phenols, methoxy phenols, ketones and fatty acids which are generally formed from pyrolysis of lignin components, such as guaiacol. The most favourable reaction step in lignin pyrolysis is the primary radical formation, which further rearranges and recombines, starting the formation of different compounds [14, 15]. Evidence from earlier study [14] demonstrates that high level of phenol compounds are either formed by recombination of guaiacol with a methyl radical or by decarbonylation of 2-hydroxybenzaldehyde, which is formed during pyrolysis of lignin.

3.3. Effect of catalyst on bio-oil deoxygenation

The addition of catalyst (Cu-zeolite or zeolite) for *in-situ* and *ex-situ* pyrolysis showed significant deoxygenation activity for alcoholic compounds and fatty acids while a considerable increase in aromatic and aliphatic hydrocarbons was achieved. It was noticed that *ex-situ* pyrolysis favoured more aromatic hydrocarbon formation as well as deoxygenation activity as compared to *in-situ* pyrolysis. In comparison, *ex-situ* pyrolysis with Cu-zeolite resulted in 41.64% aromatic hydrocarbons while *in-situ* could produce only 20.97%. The dominant aromatic hydrocarbons produced during *ex-situ* pyrolysis were pyrene (10.2%), fluorene (5.1%), and retene (3.6%) and the main aliphatic hydrocarbon was ethylidenecyclobutane, contributing 3.87% of the total bio-oil composition. Alternatively, *in-situ* pyrolysis produced phenanthrene (8.6%) and 2-isopropyl-10-methylphenanthrene (4.5%) as the main aromatic hydrocarbons while ethylidenecyclobutane was formed in almost equal concentration to *ex-situ* pyrolysis that was 3.85%. Zeolite-based catalysts generally deoxygenate the compounds through various reactions, such as cracking, decarbonylation, decarboxylation, dehydration and aromatization reactions [6, 8]. It has been known that Brønsted acid sites on zeolite surface play a pivotal role in aromatization reactions and cracking of oxygenated compounds. Besides, the introduction of Cu can increase the number of acid sites and further promote

dehydration, dehydroxylation and decarboxylation reactions [15]. Therefore, it could be urged that Cu-zeolite showed higher catalytic active sites as compared to sole zeolite and enhanced the deoxygenation activity via the various aforementioned reactions. The results also revealed that sole zeolite showed noticeable hydrocarbon production in bio-oil as compared to the bio-oil extracted from non-catalytic pyrolysis. It was observed that zeolite catalysed *in-situ* pyrolysis resulted bio-oil with 11.66% aromatic hydrocarbons while 14.2% aromatic hydrocarbons were present in bio-oil with *ex-situ* pyrolysis. In addition, the concentration of aliphatic hydrocarbons in bio-oil produced during *ex-situ* was 3.02%, which was slightly lesser to the concentration obtained with Cu-zeolite, suggesting the promising catalytic activity of sole zeolite to produce aliphatic hydrocarbons.

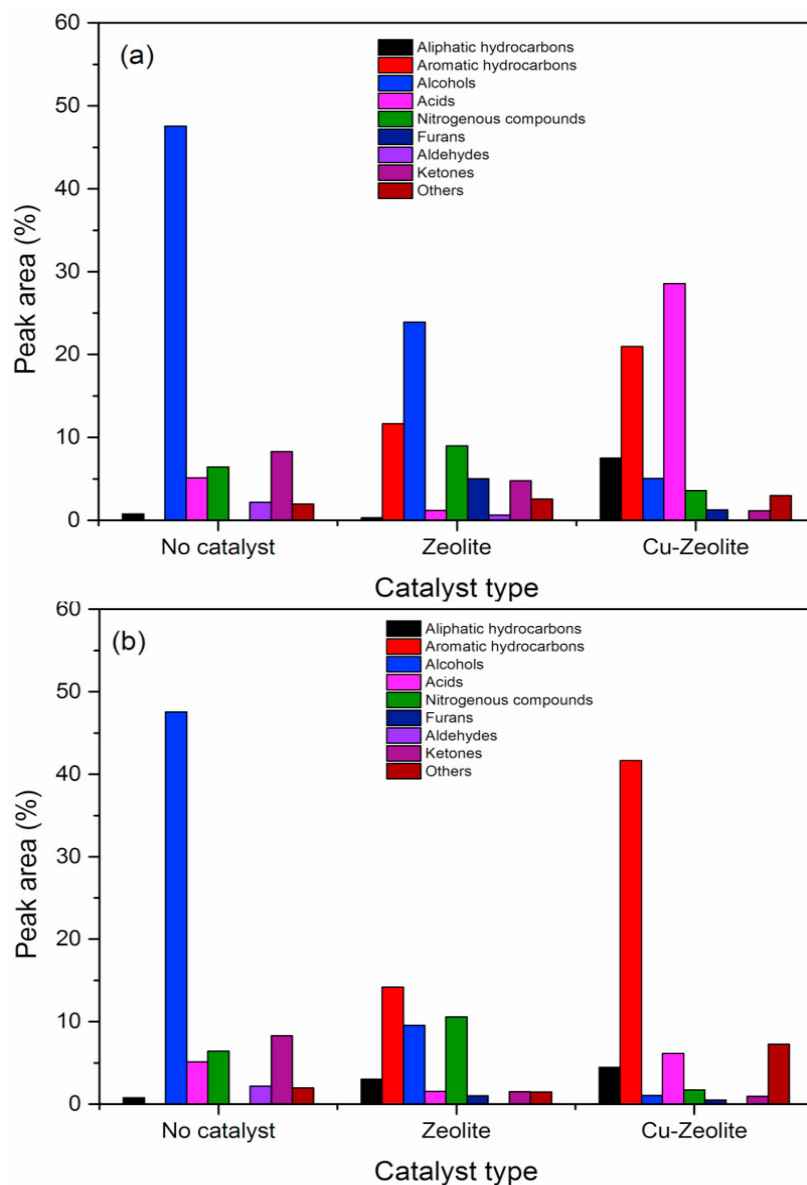


Fig. 3. Bio-oil composition from (a) *in-situ* and (b) *ex-situ* catalytic pyrolysis with and without Cu-zeolite.

On the other hand, the concentration of phenolic or alcoholic compounds obtained in bio-oil from *ex-situ* pyrolysis was only 1% and *in-situ* pyrolysis also showed a competitive reduction, producing only 5% alcoholic compounds. The second major group of oxygenated compounds during non-catalytic pyrolysis was ketones, comprising the total composition of 8.28%, which reduced to 0.97% during *ex-situ* and 1.16% during *in-situ* pyrolysis with Cu-zeolite catalyst. Another noticeable point was that sole zeolite showed a substantial decrease in fatty acids in both *in-situ* as well as *ex-situ* pyrolysis while the addition of Cu in zeolite produced fatty acids with almost similar concentration to non-catalytic pyrolysis, suggesting a negligible conversion of fatty acids to hydrocarbons. The possible reason for this could be that Cu occupied the main active sites on the zeolite surface which were responsible for the decarbonylation and decarboxylation reactions to convert fatty acids into hydrocarbons. Moreover, sole zeolite promoted the production of nitrogenous compounds (8.98% during *in-situ* and 10.58% in *ex-situ*) and furans (5%) during *in-situ* pyrolysis. However, the results demonstrated that Cu-zeolite did not favour the production of nitrogenous compounds and furans but produced more halo alkanes and thio compounds as compared to sole zeolite.

4. Conclusion

Cu-zeolite was prepared and investigated to convert the oxygenated compounds into hydrocarbons in bio-oil extracted from *in-situ* and *ex-situ* catalytic pyrolysis of pine wood sawdust. The results demonstrated that in comparison to *in-situ*, *ex-situ* catalytic pyrolysis showed significant deoxygenation activity for alcoholic compounds, ketones and fatty acids, while a considerable increase in aromatic and aliphatic hydrocarbons was achieved. Evidently, *ex-situ* pyrolysis with Cu-zeolite produced 41.64% aromatic hydrocarbons, which was approximately 193% higher than sole zeolite. Additionally, the concentration of alcohols and ketones was greatly reduced from 47.53% to 1% and 8.28% to 0.97%, respectively. This promising deoxygenation activity can be attributed to Cu-zeolite's catalytic activity that converted oxygenated compounds to refinable hydrocarbons via various reactions, such as aromatization, dehydration, decarboxylation and decarbonylation.

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