



Consequence of replacing nitrogen with carbon dioxide as atmosphere on suppressing the formation of polycyclic aromatic hydrocarbons in catalytic pyrolysis of sawdust

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ABSTRACT

This study evaluates the effect of replacement of N₂ with CO₂ as atmosphere in catalytic pyrolysis of waste lignocellulosics with acidic and metal-modified zeolites, respectively, on the 16 EPA priority pollutant polycyclic aromatic hydrocarbons (PAHs) in bio-oils. By coupling solid phase extraction pretreatment with single ion monitoring detection, it is found that the replacement alleviates PAHs in bio-oil concerning synchronously abating the 16 PAHs with low, medium and high molecular weights, and the benzo[*a*]pyrene equivalent toxicity of bio-oil decreases. Meanwhile, CO₂ decreases the content of small oxygenates, e.g. furans, ketones, acids, and increases phenolics and aromatics affording more stable and valuable bio-oils. Moreover, CO₂ enhances carbon conversion efficiency, especially in combination with Fe-modified zeolite, which presents a synergistic effect. This study indicates the practical application of CO₂ as an atmosphere in catalytic pyrolysis to improve the bio-oil quality by suppressing PAHs formation and adjusting compound constituent.

1. Introduction

The speeding-up social metabolism toward carbon, triggered by massive exploitation and utilization of fossil resources, has drawn the public acceptance for substituting renewable carbon source for traditional petro-derived fuels and chemicals. Considering the carbon neutrality, biomass such as lignocellulosics that are widely dispersed and easily accessed has been highlighted as a cost effective and promising alternative for mitigating the environmental concern resulted from greenhouse gas emission (Dabros et al., 2018; Wang et al., 2019).

Pyrolysis that occurs in the absence oxygen at elevated temperatures is an efficient route by which biomass can be converted into liquid fuels and renewably derived chemicals. This technology allows biomass to thermally decompose to smaller fragments and to form up a liquid (bio-oil) with high oxygen content and poor stability (Sharifzadeh et al., 2019). With the addition of catalysts, pyrolysis vapor is upgraded prior to condensation, and consequently a relatively more stable bio-oil with less oxygen content is obtained. This process is usually named as catalytic pyrolysis, in which the acidic zeolite such as HZSM-5 (Hoff et al., 2017; Kumar et al., 2019) and its metal modified counterparts (Li et al.,

2017; Li et al., 2016; Mullen and Boateng, 2015) are commonly applied as the catalyst because of their good capabilities for deoxygenating pyrolysis vapor and producing aromatic-rich bio-oil.

However, the use of zeolite catalysts is a double-edged sword. For example, an increase in valuable aromatics typically comes along with an increase in undesired byproduct, polycyclic aromatic hydrocarbons (PAHs). PAHs are a group of persistent organic contaminants with more than two aromatic rings, most of which are teratogenic, mutagenic, carcinogenic, etc., and therefore they are extremely harmful for health (Mahler et al., 2012). As a result, the exposure of bio-oil, e.g. during its storage, handling, or transportation, would pose potential risks for human and ecosystem. For monitoring purposes, the U.S. Environmental Protection Agency (EPA) has made a list of 16 unsubstituted PAHs that are on a priority pollutant list. In addition, PAHs in bio-oil can also cause major challenges in downstream post-processing reactors and decrease the overall carbon conversion efficiency of the process (Stark & Ghoniem, 2017). Nevertheless, most literatures concerning the topic of PAHs produced from biomass pyrolysis focused on the PAHs adhered to solid residues or particulate matters released (Dandajeh et al., 2018; Ko et al., 2018; Konczak et al., 2019), and fewer efforts

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have been devoted to analyze these PAHs that bio-oil contained. Zhou et al. (2014a) conducted the pyrolysis of xylan, cellulose and lignin at a gasification temperature (800 °C), and found the existence of ten species of PAH from the EPA priority list in bio-oil, which contained no more than four aromatic rings. Dunnigan et al. (2017) examined the bio-oil produced at 500 °C, of which the results indicated that there were only two and three ring EPA PAHs. While, similar findings were reported in the studies on spent coffee grounds (Nguyen et al., 2019). However, these researches merely involved the PAH individuals with lower molecular weights among the 16 EPA priority pollutant PAHs and concerned the bio-oil from traditional pyrolysis of biomass without the presence of any catalyst. In fact, it is highly significant to earn an intact cognition for all the 16 PAHs in bio-oil, since most of the PAHs with higher molecular weights, such as benzo[a]pyrene, which typically emerge in trace amount and hardly to be detected, are extremely toxic.

Recently, Kwon and coworkers proposed that by replacing N₂ with CO₂ as the atmosphere in traditional pyrolysis, the formation of PAHs could be effectively mitigated. They have developed a number of investigations on different feedstocks, e.g. sewage sludge (Kim et al., 2019a), polyvinyl chloride (Lee et al., 2018), municipal solid waste (Lee et al., 2017a), printed circuit board (Lee et al., 2017b), styrene butadiene rubber (Kwon et al., 2012), etc., confirming the suppression impact of CO₂ atmosphere on PAHs formation. Similarly, the thermal decomposition of lignin, a typical component of lignocellulosic biomass, at a gasification temperature (800 °C) under N₂ and CO₂ atmospheres, also revealed that the content of PAHs that existed in bio-oil produced under CO₂ atmosphere was relatively lower in comparison with under N₂ atmosphere (Zhou et al., 2014b). Apart from the effect on the PAHs suppression, it has been also found the presence of CO₂ can attract a few variations in bio-oil composition. The pyrolysis of corncob under CO₂ atmosphere was likely to provide a more stable bio-oil that contained less methoxy groups with respect to under N₂ atmosphere (Zhang et al., 2011). Mante et al. (2012) further corroborated those findings by using ¹³C nuclear magnetic resonance technique. They additionally found that the presence of CO₂ atmosphere led to increased deoxygenation reactions, which resulted in the reduction of the relative content of not only methoxyls, but also sugars, carboxylics and carbonyls. In addition, through the studies on the pyrolysis of medicinal herb residue, Zhang and Zhang (2017) concluded that the use of CO₂ as the atmosphere could also arise the hydrocarbon content in bio-oil.

In the light of these previous studies, we assumed that by substituting CO₂ for traditional inert gas N₂ as the atmosphere, catalytic pyrolysis over zeolites commonly conducted at a lower temperature (~500 °C) can also give rise to a bio-oil with limited content of PAH pollutants and, accordingly, experiments were performed to explore the impacts of this substitution. The obtained bio-oil was handled with solid phase extraction pretreatment followed by gas chromatography paired with spectrometer (GC-MS) analysis at single ion monitoring (SIM) detection mode to avoid strong interference during detecting process resulted from organic compounds such as phenolics (Fabbri et al., 2010). This analysis method as a result ensured the determination of all the 16 EPA priority pollutant PAHs in bio-oil, especially for the species with high molecular weights that mostly exist at trace levels but with high toxicities. In this way, the variation of the 16 PAHs in bio-oil with the substitution of CO₂ for N₂ as the atmosphere in catalytic pyrolysis is first time fully revealed, as well as the benzo[a]pyrene

equivalence toxicity of the bio-oil. At the same time, the constituent of effective chemical compound that existed in bio-oil produced under CO₂ in reference to N₂ was also compared. For fundamental study, a lab-scale pyrolysis of *Fraxinus mandschurica* sawdust, a commonly available waste lignocellulosics from furniture manufacturing industry in China, under N₂ or CO₂ atmosphere was carried out. The widely used zeolites HZSM-5 and its transition metal modifications were applied as the catalysts in this study.

2. Materials and method

2.1. Materials and catalyst preparation

Fraxinus mandschurica sawdust was collected from a furniture factory in Panyu district, Guangzhou city, China. Commercial protonated ZSM-5 zeolite (HZSM-5) from Nankai University Catalyst with SiO₂/Al₂O₃ ratio of 25 was calcined at 550 °C for 4 h to eliminate organic compound and moisture content before use. Transition metal Fe and Co modified HZSM-5 zeolite catalysts was prepared by incipient impregnation using Fe(NO₃)₃ and Co(NO₃)₂, respectively, achieving 10 wt% metal loading in each case, and followed by drying at 70 °C overnight. The solids were subsequently calcined at 550 °C in air for 4 h, and then reduced at the same temperature by N₂/H₂ (volume ratio 9:1) for 2 h. Proximate analysis including moisture (M), ash, volatile matter (VM), and fixed carbon (FC) of the samples, was performed according to the American Society for Testing and Materials (ASTM) D1762-84. Ultimate analysis, including carbon, hydrogen, and nitrogen, was carried out using an elemental analyzer (Vario EL cube, Elementar). The hemicellulose and cellulose components of *Fraxinus mandschurica* sawdust were quantitatively determined by the method of ASTM D5896-96, and the quantity of the lignin component was identified by ASTM D1106. The results for these basic analyses on the biomass feedstock are shown in Table 1.

2.2. Catalyst characterization

The crystal structure of the catalysts was characterized via X-ray diffraction (XRD) analysis by Cu K α radiation at a scan rate of 6°/min with a step of 0.02° in the 2 θ angle ranging from 5° to 50° performed on Bruker D8 Advance X-ray diffractometer. The nature of the acid sites on catalyst was studied by Fourier transform infrared spectroscopy (FTIR) of adsorbed pyridine on a PerkinElmer Frontier FTIR spectrometer. The catalyst sample was first finely grounded in an agate mortar and pressed into a ca. 20 mg self-supporting wafer (13 mm of diameter) in the absence of binder, which was then placed in an in situ infrared cell with CaF₂ windows. Before the measurements, all samples were treated under vacuum (10⁻² Pa) at 400 °C for 2 h and then cooled to room temperature. Spectra of the pretreated samples were collected as background. Next, pyridine was introduced to the in situ IR cell where the samples were saturated for 1 h at room temperature. The sample was then evacuated for 10 min to remove the unadsorbed pyridine. The desorption of the pyridine was successively monitored stepwise, by evacuating the sample for 30 min at 350 °C, and cooling to room temperature to record the spectrum. The difference spectrum was obtained by subtracting the background spectrum that was previously obtained. Textural properties of the catalyst involving specific surface

Table 1
Basic analysis of *Fraxinus mandschurica*.

Proximate analysis (wt.%)				Ultimate analysis (wt.%)					Component analysis (wt.%)		
M	Ash	VM	FC ^a	C	H	O ^a	N	S	Cellulose	Lignin	Hemicellulose
0.60	0.92	83.17	15.31	46.03	6.07	46.88	0.03	0.99	40.63	30.20	29.17

^a Acquired by subtraction.

area, and pore size and volume of the catalysts were determined by Micromeritics ASAP 2020 Plus HD88 analyzer. The nitrogen adsorption/desorption isotherms were conducted at $-196\text{ }^{\circ}\text{C}$. Brunauer-Emmett-Teller (BET) method and Barret-Joyer-Halenda (BJH) method were adopted for analyzing the specific surface area and pore size and volume, respectively.

2.3. Pyrolysis experiment

The catalytic pyrolysis was performed in a tubular reactor at $500\text{ }^{\circ}\text{C}$. In each run, $\sim 4\text{ g}$ of *Fraxinus mandschurica* sawdust and catalyst or quartz sand mixture at the ratio of 1:1 in weight was loaded in a quartz boat which was then pushed into the heating zone of the tubular reactor when the set temperature was reached. A constant N_2 or CO_2 with 300 mL/min was introduced during the pyrolysis to create a relatively inert atmosphere and carry volatile products out. A catalytic pyrolysis experiment using HZSM-5, Fe/HZSM-5, and Co/HZSM-5 zeolites under N_2 atmosphere is denoted as $\text{N}_2\text{-HZ}$, $\text{N}_2\text{-Fe/HZ}$, and $\text{N}_2\text{-Co/HZ}$, respectively; similarly, the use of them under CO_2 atmosphere is denoted as $\text{CO}_2\text{-HZ}$, $\text{CO}_2\text{-Fe/HZ}$, and $\text{CO}_2\text{-Co/HZ}$, respectively. A set of methanol absorption bottle was placed in an ice bath to condense organic substances. After 5 min reaction, the quartz boat was pushed out from the heating zone and the solid residues (bio-char) were cooled down to room temperature under inert atmosphere. Then, the methanol solutions of bio-oil were collected and saved in a refrigerator at $3\text{ }^{\circ}\text{C}$ for analysis.

2.4. Bio-oil pretreatment and analysis

The bio-oil solutions was undergone several pretreatment procedures for the analysis of the 16 EPA priority pollutant PAHs. The solution was first dried by anhydrous sodium sulfate overnight. 5 species of deuterated PAHs (AccuStandard, USA), i.e., naphthalene- D_8 , acenaphthene- D_{10} , phenanthrene- D_{10} , chresene- D_{12} , and perylene- D_{12} , were spiked into the solution as recovery indicators for the 16 PAHs with different vapor pressures (Table 2) to evaluate their loss caused by the subsequent treatments. The sample was then rinsed by the solution of n-hexane and dichloromethane mixture in the volume ratio of 7:3, and purified by flowing through a silica gel and alumina packed column. Next, the eluate collected at the bottom of the column was

Table 2
Characteristics of priority pollutant PAHs regulated by EPA.

PAH compound	Abbreviation	No. of rings	Vapor pressure ^a (Pa, $25\text{ }^{\circ}\text{C}$)	TEF ^b
Naphthalene	Nap	2	11.14	0.001
Acenaphthylene	Acp	3	3.87	0.001
Acenaphthene	Ace	3	3.07	0.001
Fluorene	Flu	3	1.66	0.001
Phenanthrene	PhA	3	1.06×10^{-1}	0.001
Anthracene	Ant	3	8.60×10^{-4}	0.01
Fluoranthene	FluA	4	8.61×10^{-4}	0.001
Pyrene	Pyr	4	5.00×10^{-5}	0.001
Benzo[a]anthracene*	BaA	4	5.43×10^{-4}	0.1
Chrysene*	Chr	4	4.00×10^{-6}	0.01
Benzo[b]fluoranthene*	BbF	5	5.00×10^{-7}	0.1
Benzo[k]fluoranthene*	BkF	5	5.20×10^{-8}	0.1
Benzo[a]pyrene*	BaP	5	6.00×10^{-8}	1
Dibenzo[ah]anthracene*	DbA	5	1.33×10^{-8}	1
Indeno[123-cd]pyrene*	IcP	6	1.27×10^{-7}	0.1
Benzo[ghi]perylene	BgP	6	1.38×10^{-8}	0.01

* Carcinogenic PAHs.

^a According to (Odabasi et al., 2006).

^b Toxicity equivalent factor (TEF) refers to the toxicity of each PAH species compared to that of benzo[a]pyrene which is the highest equal to 1 (Nisbet and Lagoy, 1992).

concentrated to $\sim 1\text{ mL}$ by rotary evaporation and N_2 blowing evaporation, which was then the bio-oil sample adapted to PAHs analysis. Before the analysis of PAHs, hexamethylbenzene (Ehrenstorfer-schafer Bgm-Schlösser Laboratory, Germany) was added as the internal standard.

The 16 PAHs were analyzed by gas chromatography (Agilent 7890B) paired with mass spectrometry (Agilent 5977B) (GC-MS) using selected ion monitoring (SIM) mode. The primary and secondary selected ions for the 16 PAHs, the 5 deuterated PAHs (dPAHs), and the internal standard hexamethylbenzene were determined according to EPA method 8270E (SW-846). In this study, HP-5MS ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$, Agilent) capillary column was used for separation purpose in GC-MS analysis. The temperature program of capillary column oven for the PAHs analysis was held at $80\text{ }^{\circ}\text{C}$ for 1 min first; then increased to $160\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C/min}$; increased to $220\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C/min}$ and, finally increased to $310\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C/min}$ and held for 5 min. Quantitative analysis of the 16 PAHs was conducted against a calibration curve generated by injecting a series of mixed PAHs standard solutions (Ehrenstorfer-schafer Bgm-Schlösser Laboratory, Germany) of which the concentration ranged from 200 to $1000\text{ }\mu\text{g/L}$. Three duplicate test were performed, and the recoveries indicated by the 5 dPAHs ranging from 75% to 110% for all tested samples with relative standard deviation in the range of 4% to 11.5%.

Besides, the bio-oil solution after drying was directly used for semi-quantitative analysis of chemical composition via GC-MS. The MS was set to be at scanning mode in the range of 30–500 amu. While, the temperature program of the oven was held at $35\text{ }^{\circ}\text{C}$ for 8 min first; then increased to $100\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C/min}$ and held for 3 min; increased to $220\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C/min}$, and finally increased to $290\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C/min}$ and held for 5 min. The results were acquired by integrating the relative area of peaks appeared at different retention times according to the total ion chromatogram.

3. Results and discussion

3.1. Catalyst characterization

To check the potential structure changes of the zeolite framework after the metal modification, XRD analysis was carried out. The related XRD patterns corroborate the preservation of ZSM-5 zeolite structure in metal modified samples, consistent with the earlier reports (Li et al., 2017; Li et al., 2016). The XRD peaks of metal crystals are hardly seen in these patterns. The absence of the peaks of Fe or Co metal material suggests that these species should be well-dispersed in the zeolite support. On the other hand, a deviation is observed with respect to the intensity of the featuring peaks of ZSM-5: the peaks become smaller after metal addition, which is possibly due to the decrease in the proportion of ZSM-5 crystalline phases in a metal modified zeolite. Li et al. (2017) found a similar result in their research on HZSM-5 zeolite catalyst modified by several metals.

Pyridine (Py) has been proved to be an appropriate probe molecule to test the acidic characteristics of zeolite solids. The merit of its use is that the molecule adsorbed on Brønsted and Lewis acid sites affords IR bands at different wavenumbers, and thus it renders the differentiation of these sites. However, it is noteworthy that the Py-IR results can only give semi-quantitative information towards the variation in amount for both sites rather than precise quantification. The Py-IR spectrum was recorded at $350\text{ }^{\circ}\text{C}$ after weakly adsorbed pyridine was removed by evacuation at the same temperature. The band at 1545 cm^{-1} and 1450 cm^{-1} corresponds to the pyridine adsorption on Brønsted and Lewis acid sites, respectively. The numerical values of integrated intensities (A_{int}) are listed in Table 3. It is found that the HZSM-5 zeolite exhibits Brønsted acidity only. However, the nature of the acidity changes with the loading of the transition metal Fe or Co. Lewis acidity starts to exist in the Fe modified HZSM-5 zeolite, with the Brønsted/Lewis (B/L) ratio of 3.51, and this ratio sharply declines to 0.34 for the

Table 3
Textural and acidic characteristics of catalysts.

Catalyst	N ₂ adsorption/desorption			Py-IR	
	S _{BET} (m ² /g)	D _{pore} (nm)	V _{total} (mL ³ /g)	Brønsted A _{int} ^a (cm ⁻¹)	Lewis A _{int} ^a (cm ⁻¹)
HZSM-5	295.93	1.35	0.20	0.28	n.d.
Fe/HZSM-5	274.67	1.35	0.18	0.13	0.03
Co/HZSM-5	229.81	1.32	0.16	0.03	0.10

^a S_{BET} denotes specific area.

^b V_{total} denotes total pore volume.

^c D_{pore} denotes average pore diameter.

^d A_{int} denotes integrated intensity of Py-IR signal.

Co metal modification. As shown in table 3, compared to Fe/HZSM-5, Co/HZSM-5 zeolite is further more Lewis acidic and much less Brønsted acidic, of which the trend is in accordance with the findings for the addition of Fe and Co on MCM-41 zeolites (Szegeedi et al., 2004). At the impregnation step in a metal modification treatment, metal cations are prone to be anchored at a Brønsted acid site that owns a proton, which may accordingly cause the replacement for the proton or the coverage over the Brønsted acid site with the metallic species (Bernardon et al., 2017), and thus causes decrease in Brønsted acidity and increase in Lewis acidity.

The results obtained from N₂ adsorption/desorption isotherms are listed in Table 3. It shows that specific surface areas diminish after the addition of Fe and Co, leading to ca. 7% and 22% decrease, respectively. This suggests the appearance of the metal species inside the porous ZSM-5 network (Iliopoulou et al., 2012), which is also reflected by the decrease in total pore volume. However, the average pore diameters are nearly identical for all the samples so that the shape selectivity of the channels may be less affected by the metal loadings (Xu et al., 2017).

3.2. Composition of bio-oils

The relative content of different group of chemical compounds in liquid products collected from *Fraxinus mandshurica* pyrolysis with and without catalysts over zeolites under N₂ and CO₂ atmosphere is shown in Fig. 1. Six groups of chemical compounds were categorized, including furans, phenols, aromatics, ketones and miscellaneous oxygenates (mis-oxy). Phenols and furans are the most abundant groups in

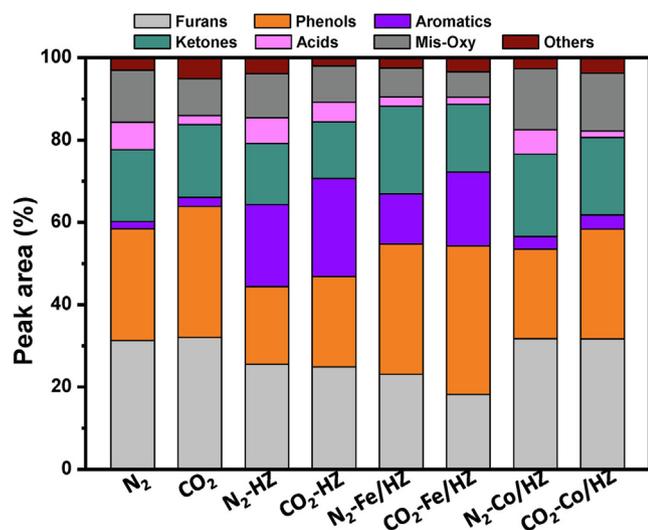


Fig. 1. Content of different chemical species in bio-oils produced under N₂ and CO₂ atmospheres with HZSM-5, Fe/HZSM-5 and Co/HZSM-5 zeolite catalyst and without catalyst.

the bio-oils, accounting for 18.81–36.06% and 18.19–32.00%, respectively. The content of aromatics, ketones, and acids are 1.78–23.84%, 13.75–21.30%, and 1.57–6.64%, respectively. Aldehydes and alcohols are involved into the category of miscellaneous oxygenates, which is in the range of 6.15 to 12.64%.

Aromatics are most value-added chemical compound within bio-oil from catalytic pyrolysis with zeolite, since they can be directly used as liquid fuel additives (Lu et al., 2018a; Lu et al., 2018b; Zhang and Zhang, 2017). Apparently, the use of HZSM-5 and Fe/HZSM-5 zeolite leads to an increase in aromatics, while this effect is less significant for Co/HZSM-5 zeolite. Under N₂ atmosphere, the highest content of aromatics 20.00% is achieved via applying HZSM-5 owing to its stronger Brønsted acidity and higher surface area, followed by Fe/HZSM-5 (12.19%), and the content is only 3.05% for the application of Co/HZSM-5, which is comparable to the amount in the bio-oil obtained from the pyrolysis without zeolite. This observation indicates that HZSM-5 is more effective than are its metal modified counterparts for the formation of aromatics. The findings from Mullen and Boateng (2015) also presented that the addition of transition metals on HZSM-5 would suppress the formation of aromatics, and HZSM-5 had a higher production rate than its iron modification when it came to aromatics. By replacing N₂ with CO₂ as the catalytic pyrolysis atmosphere, the bio-oils are more aromatic. Particularly, the increase in aromatics is most obvious when using HZSM-5 and Fe/HZSM-5 zeolite catalysts. They have a relative content of 23.84% and 18.01%, which corresponds to ca. 1.2 and 1.5 times more than the amount of aromatics observed in N₂ atmosphere, respectively. Hence, it can be said that CO₂ atmosphere is able to enhance the formation of aromatics. This observation is coherent in the light of studies led by Mante et al. (2012): participation of CO₂ in pyrolysis atmosphere results to the increase in total aromatics. They ascribed this phenomenon to the capability of CO₂ for suppressing coke formation and reducing carbon deposits on the catalyst resulting in its better catalytic performance. Prior studies on conversion of methanol to aromatics also corroborated the positive impact of CO₂ on the aromatization reaction over zeolite (Xu et al., 2017). They claimed that zeolite is capable of activating the CO₂ absorbed on its surface as a hydrogen receptor to prevent the olefin intermediates from forming paraffins by hydrogenation, thus facilitating the yield of aromatics.

Phenols are an important chemical family for industrial. For example, they are starting materials to make plastics, explosives such as picric acid, and drugs such as aspirin. In this study, phenolics are one of the most abundant species, which can be possibly resulted from that phenolics are mainly derived from thermal decomposition of lignin component of biomass, of which the content is as high as ~30 wt% in *Fraxinus mandshurica* as shown in Table 1. Under N₂ atmosphere, the use of HZSM-5 zeolite leads to the fewest phenols (18.81%) in bio-oil compared to the cases with Co/HZSM-5 (21.76%) and Fe/HZSM-5 (31.67%) catalyst, and without any catalyst (27.09%). As for the effect of reaction atmosphere, CO₂ seems to have enhanced phenols formation since their content shows an increase in peak area in comparison with N₂. These findings are consistent with the literature where phenols have been reported to increase in bio-oils from the pyrolysis of switchgrass with substituting CO₂ for N₂ as the atmosphere (Pilon & Lavoie, 2013). Besides, similar to the trend in N₂ atmosphere, Fe/HZSM-5 exhibits the best performance for phenols yield under CO₂ atmosphere, corresponding to the relative peak area of 36.06%, followed by Co/ZSM-5 at the value of 26.68% that is slightly less than the case without catalyst (31.85%). The worst performance for phenols yield under CO₂ atmosphere is also presented by HZSM-5 giving a relative peak area of 21.96%.

In parallel, the content of furans, ketones, carboxylic acids and other oxygenates in bio-oil is changed with the application of different catalyst and atmosphere applied in pyrolysis as well. For example, the use of HZSM-5 reduces the content of furans, and the addition of Fe on it further intensifies this reduction giving a relative peak area of 23.05% that is the lowest yield among the bio-oils obtained under N₂

atmosphere, while Co/HZSM-5 gives rise to a similar content of furans with respect to the case without catalyst. The replacement of N₂ with CO₂ generally leads to a minor abatement in the content of furans except for the catalyst of Fe/HZSM-5. Similarly, it can be also observed that the presence of CO₂ mostly gives a lower content of ketones, acids, and miscellaneous oxygenates. It is worth noting that furans, a typical category of intermediates formed via thermal fragmentation of the cellulose and hemicellulose constituents, are basically consumed by secondary degradations such as dehydration, decarbonylation, decarboxylation, oligomerization, and aromatization which are prone to occur at the Brønsted acid sites on a zeolite (Che et al., 2019). In reference to Table 3, it can be concluded that the strong Brønsted acidity of zeolite would enhance furan species conversion, which was also corroborated previously (Kumar et al., 2019). In addition, it is observed that ketones are slightly fewer with the application of HZSM-5, but then their content is increased by the use of the metal modified zeolites. Earlier studies has also reported that compared to parent HZSM-5, the modification of transition metals incurred an increase in ketones (Mohabeer et al., 2019).

The above observations signify that the substitution of CO₂ results in an enhancement for deoxygenation reactions affording a bio-oil with fewer oxygen-containing compounds. These compounds such as acids and ketones are mostly active compositions in pyrolytic bio-oil (Iliopoulou et al., 2012). Thereby, it can be inferred that to use CO₂ instead of N₂ as the pyrolysis atmosphere is able to make the bio-oil more stable. At the same time, the resulted increase in its aromatic and phenolic constituents can be associated with a more value-added bio-oil. According to the investigations on bio-oils produced from pyrolysis of hybrid poplar through ¹³C Nuclear Magnetic Resonance analysis, carboxylic and carbonyl fractions were lessened and aromatic fractions were increased in the presence of CO₂ in pyrolysis atmosphere (Mante et al., 2012), of which the result is aligned with the findings from the current study. These phenomena are plausibly due to the expedited thermal cracking of oxygenates as a result of employing CO₂, which was previously evidenced in the pyrolysis of spent coffee grounds (Kim et al., 2019b).

3.3. CO₂ suppression for PAHs

3.3.1. PAHs determination

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the environment. It is therefore important to know the content of PAHs present in bio-oil before its application. Applying solid phase extraction pretreatment combined with GC-MS single ion monitoring to the PAH analysis of bio-oil enables the detection of PAHs that occur in trace amount, in particular for PAHs with higher molecular weights often exhibiting high toxicities. The 16 EPA priority pollutant PAHs are detected in the bio-oil obtained from pyrolysis in N₂ atmosphere in the absence of catalyst, and their distribution and concentration are presented in Fig. 2. The PAHs are categorized into three groups: high molecular weight with 5–6 aromatic rings (HPAHs) involving BbF, BkF, BaP, DbA, IcP, and BgP, medium molecular weight with 4 aromatic rings (MPAHs) involving FluA, Pyr, BaA, and Chr, and low molecular weight with 2–3 aromatic rings (LPAHs) involving Nap, Acp, Ace, Flu, PhA, and Ant. These PAHs are of environmental concern due to their possible toxicity in humans and other organisms and their prevalence and persistence in the environment (Dat and Chang, 2017).

The concentration of the PAHs ranges from 0.53 to 5.29 µg/g, where naphthalene is the most abundant species while benzo[ghi]perylene possesses the least amount. This result is mostly in line with the previous findings that the 16 PAHs were in the range of 0.1 to 0.7 µg/g (Fabbri et al., 2010). In general, the content of the PAHs decreases with the increase in their molecular weight. It is noteworthy that the measurement error that shown by the error bar of each column also appears a decrease as the molecular weight of the PAHs increase, which can be immediate relevance to the vapor pressure of each species presented in

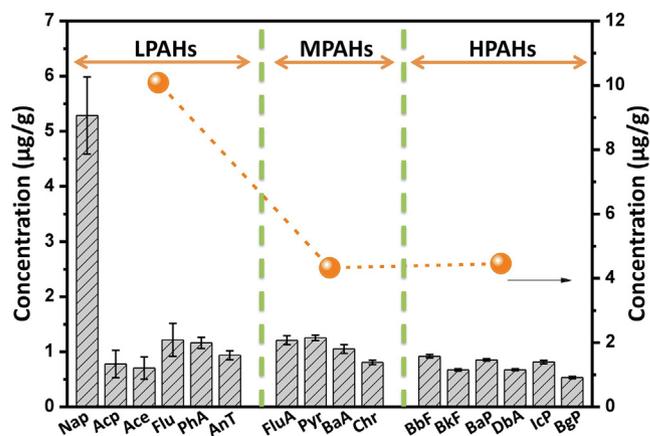


Fig. 2. Distribution and quantity of the 16 EPA priority pollutant PAHs in bio-oil produced under N₂ atmosphere without catalyst.

Table 2. In relative terms, PAHs with high vapor pressure, e.g. naphthalene, acenaphthylene, acenaphthene, fluorene, which have advanced vaporizing tendency, are less controllable in regards to the loss during bio-oil pretreatment process, and thus give rise to a relatively high error. Likewise, as the result of the variation in vapor pressure, the recoveries indicated by the deuterium labeled surrogates are ca. 80% for naphthalene-D₈ and acenaphthene-D₁₀, which represent the loss of LPAH species, and close to 100% for phenanthrene-D₁₀, chresene-D₁₂ and perylene-D₁₂ representing the loss of PAHs with higher molecular weights and lower vapor pressures. In addition, it is observed from Fig. 2 that the total PAHs of low ring is more than 10 µg/g, but the total PAHs of medium and high ring is less than half of the total PAHs of low ring. Similar trends were also previously reported by Dunnigan et al. (2017) for the bio-oil collected from pyrolysis of rice husk in N₂ atmosphere. However, their results are in a much smaller quantity (0.85–0.09 µg/g, 4–6 rings not detected). This discrepancy is possibly attributed to the nature of feedstock, the operating conditions of the reactor, for example, the reactor type and the carrier gas injection rate, and the PAH analysis method as well.

3.3.2. CO₂ effect on PAHs with different molecular weights

Fig. 3 shows the content of LPAHs, MPAHs, and HPAHs in the bio-oils produced at different catalytic scenarios under N₂ and CO₂ atmosphere, respectively. LPAHs had a much larger amount compared to MPAHs and HPAHs, giving a variation from ten to hundred, and naphthalene is always the most abundant PAH species. In contrast, the change of MPAHs and HPAHs is relatively small. Their concentration varies within the range of 1 to 5 µg/g. The predominance of naphthalene in its content among the PAH species that the bio-oil contained was also evidenced in other studies on the pyrolysis of a variety of biomass feedstocks such as lignin (Zhou et al., 2014b), pine (Li et al., 2016), palm kernel shell (Maliutina et al., 2017) and spent coffee ground (Nguyen et al., 2019). Among the given 16 EPA PAHs, benzo[a]pyrene is of the greatest concern due to its high carcinogenicity (Wang et al., 2017). Fortunately, the available data showed that benzo[a]pyrene is less available in the obtained bio-oils (< 1 µg/g), lower than the mean value (1.3 µg/g) of 48 different crude oils that most commonly apply in real practice (Kerr et al., 1999).

As for LPAHs presented in Fig. 3(a), a clear increase in their total is observed with the use of HZSM-5 catalyst, which is over 35 times more than those detected in bio-oil produced without catalyst. This significant increase could be mitigated by loading transition metals on the zeolite. For example, the LPAHs concentration decreases from 351.10 µg/g when HZSM-5 is applied, to 71.25 µg/g when the Fe-modified zeolite is applied, and it is further decreases to < 20 µg/g with the application of Co/HZSM-5 zeolite. By substituting CO₂ for N₂ as the pyrolysis atmosphere, it gives rise to a general decrease in LPAHs

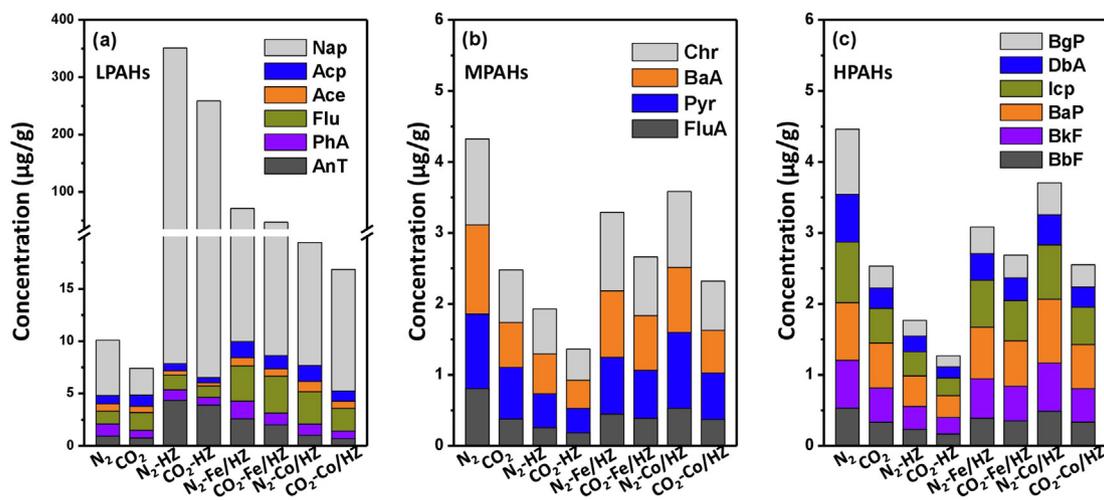


Fig. 3. Comparison of LPAHs (a), MPAHs (b), and HPAHs (c) in bio-oils produced under N_2 and CO_2 atmospheres with HZSM-5, Fe/HZSM-5 and Co/HZSM-5 zeolite catalyst and without catalyst.

Table 4
Reduction effect of CO_2 on PAHs in bio-oil.

Parameter ^a	CO_2 vs. N_2	CO_2 -HZ vs. N_2 -HZ	CO_2 -Fe/HZ vs. N_2 -Fe/HZ	CO_2 -Co/HZ vs. N_2 -Co/HZ
LPAHs-D ($\mu\text{g/g}$)	2.68	92.33	24.16	2.56
LPAHs-P	26.59%	26.30%	33.92%	13.18%
MPAHs-D ($\mu\text{g/g}$)	1.84	0.57	0.63	1.26
MPAHs-P	42.67%	29.37%	19.11%	35.17%
HPAHs-D ($\mu\text{g/g}$)	1.93	0.50	0.40	1.16
HPAHs-P	43.22%	28.19%	12.88%	31.21%
Σ PAH16-D ($\mu\text{g/g}$)	6.45	93.39	25.19	4.98
Σ PAH16-P	34.20%	26.32%	32.45%	18.63%
Σ PAH7-D ($\mu\text{g/g}$)	2.48	0.64	0.54	1.58
Σ PAH7-P	42.91%	28.07%	13.72%	32.76%
TEQ-D	0.71	0.32	0.22	0.56
TEQ-P	37.49%	26.79%	14.18%	31.44%

^a LPAHs-D, MPAHs-D, HPAHs-D, Σ PAH16-D, Σ PAH7-D, and TEQ-D are reduction amounts equal to the value in CO_2 minus the value in N_2 , respectively; LPAHs-P, MPAHs-P, HPAHs-P, Σ PAH16-P, Σ PAH7-P, and TEQ-P are reduction percentages equal to the value of reduction amount divided by the value in N_2 .

concentration. As presented in Table 4, the substitution reduces the LPAHs production catalyzed by Fe/HZSM-5 most, arriving at $\sim 35\%$ reduction, which corresponds to the absolute reducing amount of 92.33 $\mu\text{g/g}$. While from Fig. 3(b) and 3(c), it is found that the total amount of MPAHs and HPAHs in bio-oil is quite low ($< 5 \mu\text{g/g}$) in reference to LPAHs, which complies with the findings reported by Alhroub et al. (2018) who also claimed that PAH species with higher membered rings is hard to be formed for a short thermal treatment time. In some detail, a decrease of MPAHs and HPAHs is generally observed with the addition of catalysts, and particularly the use of HZSM-5 zeolite reduces their concentrations to the level of $< 2 \mu\text{g/g}$. Again, the presence of CO_2 brings about a detrimental effect on the both PAH categories. For example, the substitution of N_2 by CO_2 as an atmosphere leads to nearly a half reduction in the total amount of MPAHs and HPAHs, respectively, in the absence of catalyst.

As a result, it can be said that the use of CO_2 instead of N_2 as an atmosphere leads to a synchronous reduction in the concentration of LPAHs, MPAHs, and HPAHs in bio-oil obtained from the pyrolysis of Fraxinus mandschurica biomass no matter with or without catalyst. At the same time, it is worth underlying that two- and three-ringed PAHs can easily dissolve in bio-oil, while PAHs with higher molecular weights are prone to adhere to particular matter such as carbon residues and zeolite solids during pyrolysis (Ramesh et al., 2004). This

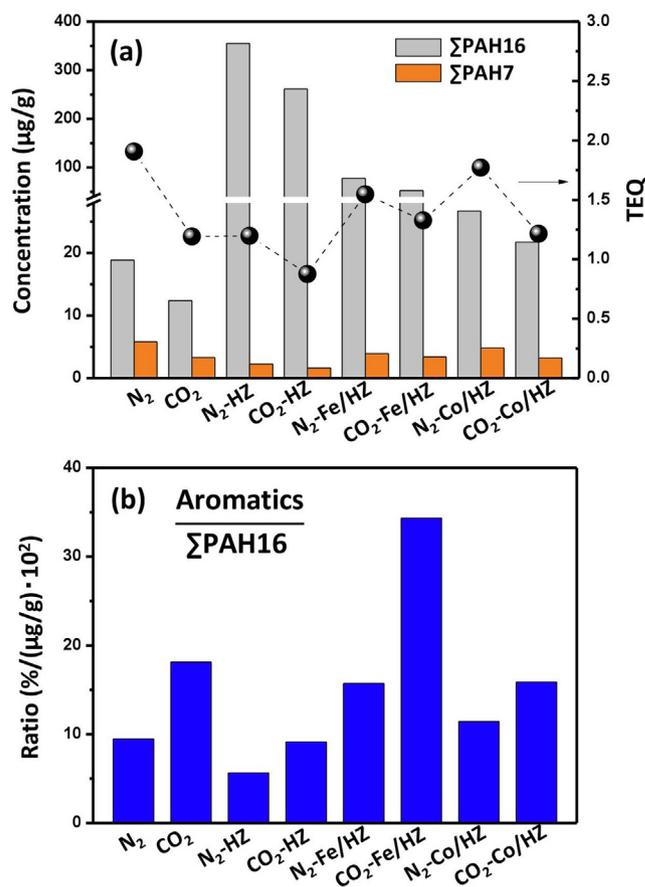


Fig. 4. Σ PAH16, Σ PAH7 and TEQ of the 16 EPA priority pollutant PAHs (a); ratio of aromatics against the sum of EPA 16 priority pollutant PAHs (b).

could be a part of the reason for the decline in the content of MPAHs and HPAHs in bio-oils with the use of zeolite catalysts.

3.3.3. CO_2 effect on toxicity and carbon conversion efficiency

In Fig. 4(a), the gray and orange columns stand for the sum of the concentrations of 16 EPA priority pollutant PAHs (Σ PAH16) and 7 carcinogenic PAHs (Σ PAH7), respectively, and the black dots represent the toxic equivalence quotient (TEQ) of the 16 PAHs, i.e. the benzo[a]pyrene equivalence toxicity of bio-oil, where $TEQ = \Sigma(\text{PAH}_i \times \text{TEF}_i)$

in which PAH_i and TEF_i denotes the concentration and TEF of a certain PAH species, respectively. Obviously, the addition of zeolite catalysts causes a significant increase in ΣPAH₁₆ of which the amount followed the order HZSM-5 > Fe/ZSM-5 > Co/ZSM-5 under both N₂ and CO₂ atmospheres. This trend is similar to the trend observed in Fig. 3(a) for LPAHs, implying the substantial contribution of the LPAHs content towards the total amount of the 16 PAHs. Conversely, zeolite catalysts have limited impact on the values of ΣPAH₇ which are all below 6 μg/g, where a decrease can be even observed. Accordingly, it is further confirmed that the addition of zeolite catalysts favors the formation of LPAHs most, especially for the yield of naphthalene. On the other hand, TEQs of the bio-oils are relatively stable, retaining at the level below 2, which indicates that the toxicity of the bio-oils is practically impervious to the use of catalysts. This observation can be resulted from two aspects of consideration. First, although the increase in LPAHs is significant, they are less toxic PAH species (Table 2) that only have a minor contribution to the value of TEQ. Moreover, the concentrations of MPAHs and HPAHs slightly decreases in the presence of zeolite catalysts (Fig. 3(b) and (c)), which thereby negatively contribute to the value of TEQ. It should be noted that although most HPAHs are carcinogenic species with much higher TEQ, the LPAHs and MPAHs are as serious threats to human health as HPAHs, since PAHs with two to four aromatic hydrocarbon rings, are more potent as co-carcinogens at the promotional phases of cancer (Ramesh et al., 2004). To this end, the reduction of the amount of the 16 PAHs and the 7 carcinogenic PAHs are of equivalent significance. Clearly, the replacement of N₂ with CO₂ as pyrolysis atmosphere gives rise to a decrease in the values of ΣPAH₁₆, ΣPAH₇, and TEQ by more than 25% in most cases as shown in Table 4. This additionally indicates that CO₂ atmosphere possess the ability to inhibit the formation of PAHs no matter whether zeolite catalysts are applied, consequently reducing the toxicity of the bio-oils.

ZSM-5 zeolite that owns MFI topology is good at producing value-added chemicals such as aromatics in biomass pyrolysis, but it always comes along with PAH byproducts (Lu et al., 2018a; Lu et al., 2018b; Zhang and Zhang, 2017). PAHs formed through biomass pyrolysis are not only a source of toxicity but also important precursors of coke or carbonaceous species, which as a result decreases carbon conversion efficiency and causes catalyst deactivation (Stark and Ghoniem, 2017). In current study, the carbon conversion efficiency under different circumstance is evaluated by introducing a factor that equals the ratio of the relative area of aromatics against the total concentration of the 16 PAHs (η_c). As shown in Fig. 4(b), the addition of zeolite catalyst generally reduces η_c into a half, while it is increased by substituting CO₂ for N₂ as the atmosphere. The maximum η_c appears at the situation of the addition of Fe/ZSM-5 zeolite by using CO₂ as the pyrolysis atmosphere, corresponding to the value of η_c that is over 3 times higher with respect to the case of traditional pyrolysis under N₂ atmosphere without any catalyst. In light of this phenomenon, it is reasonable to speculate that there is a certain synergetic effect of CO₂ and Fe-modified HZSM-5 zeolite on biomass pyrolytic conversion.

Unlike feedstocks such as sewage sludge (Hu et al., 2019; Ko et al., 2018) and electronic waste (Lee et al., 2017b; Soler et al., 2018), lignocellulosic biomass itself does not originally contain PAHs. As a result, the PAHs that observed in bio-oil can be only formed during the thermochemical process in catalytic pyrolysis. For example, a variety of PAHs are possibly produced from benzene derivatives formed by aromatization of olefins and reduction of phenolics, through the Diels-Alder reaction and hydrogen radical abstraction-acetylene addition pathways (Kislov et al., 2005). It is thereby inferred that the presence of CO₂ atmosphere potentially impedes dehydrogenation that occurs in a homogeneous process, further resulting in an inhibition effect on addition reactions by which PAHs are typically formed. Previous studies have corroborated that CO₂ atmosphere can effectively suppress dehydrogenation of pyrolysis vapor evolved from the pyrolysis of orange peel by random bond scissions (Kwon et al., 2019). The authors further proposed that the formation of PAHs can be also alleviated by the

reactions between CO₂ and volatile organic compounds (Kim et al., 2019a; Lee et al., 2017a; Lee et al., 2017b; Lee et al., 2018). All experimental findings in this study indicate the practical application of CO₂ as an atmosphere during catalytic pyrolysis to enhance the conversion efficiency of thermochemical processes, and the strategical means to suppress PAH species referring as environmental pollutants.

4. Conclusion

Combinations of CO₂ atmosphere with zeolites in catalytic pyrolysis of sawdust were evaluated concerning the 16 EPA PAHs. The replacement of N₂ with CO₂ caused a synchronous decrease in LPAHs, MPAHs and HPAHs, and thus abated the ΣPAH₁₆ and ΣPAH₇ in bio-oil and its toxicity. CO₂ led to higher carbon conversion efficiency, which reached the maximum synergized with Fe/HZSM-5 zeolite, doubled in comparison with N₂. Moreover, furans, ketones and acids decreased, and phenolics and aromatics increased in bio-oil under CO₂, exhibiting intensified deoxygenation impact. This study experimentally validated the promoting effect of CO₂ on the quality of bio-oil from catalytic pyrolysis with zeolites.

CRedit authorship contribution statement

Yao He: Conceptualization, Methodology, Writing - original draft. **Si Chen:** Investigation, Formal analysis. **Junjie Chen:** Data curation, Visualization. **Dongxia Liu:** Supervision, Validation. **Xunan Ning:** Funding acquisition, Resources. **Jingyong Liu:** Project administration. **Tiejun Wang:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2019.122417>.

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