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Migration/transformation characteristics of heavy metals and polycyclic aromatic hydrocarbons in the co-liquefaction treatment of pig manure and lignocellulosic biomass

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ABSTRACT

The migration/transformation characteristics of heavy metals and polycyclic aromatic hydrocarbons (PAHs) during the co-liquefaction of pig manure and rice straw/wood sawdust were explored in this study. More than 87% of the heavy metals in feedstocks were enriched in hydrochars. The decreased proportion of active heavy metals in the hydrochars suggested partial passivation of the heavy metals. The pollution degree and risk of heavy metals were significantly mitigated from high and considerable levels in pig manure to moderate and low levels in hydrochar, respectively. Compared with commercial diesel, bio-oil products still contained an undesirable amount of heavy metals. PAHs were re-synthesized during liquefaction, with a net synthesis amount of 29.65–73.98 $mg \cdot kg^{-1}$. Moreover, the PAHs mainly existed in bio-oils, with a content of 57.32–132.33 $mg \cdot kg^{-1}$ and a toxicity equivalent of 3.25–8.19 $mg \cdot kg^{-1}$. Compared to pig manure, the hydrochars presented a lower content of PAHs (1.76–3.53 $mg \cdot kg^{-1}$ *versus* 3.73 $mg \cdot kg^{-1}$) and a smaller toxicity equivalent (0.14–0.22 $mg \cdot kg^{-1}$ *versus* 0.26 $mg \cdot kg^{-1}$). Interestingly, introducing lignocellulose (especially for rice straw) during the liquefaction of pig manure further mitigated the pollution degree/risk of heavy metals and PAHs. Overall, hydrochar reached a safe utilization level, while bio-oil products needed further clarification.

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1. Introduction

Human society is constantly developing and advancing, with the consumption of animal-based food increasing. Pork is one of the most widely consumed meat products globally, with an annual output of 128 million tons. China has the largest pork consumption level, accounting for 38.8% of the global total [1]. Presently, the widely adopted intensive farming model has brought about new environmental problems, such as a large amount of pig manure (PM) that cannot be immediately consumed by the surrounding environment and that requires professional centralized processing. In China, the annual output of PM has reached 1.9 billion tons [2]. Notably, the treatment or disposal of PM should adopt a resource-recycling approach, considering that a large amount of organic matter and nutrients exist in PM [3]. Meanwhile, it should be noted that PM also contains a certain amount of environmental contaminants, such as heavy metals, harmful bacteria, antibiotics, *etc.* [4,5]. Inappropriate management of PM can easily lead to the pollution of soil, the atmosphere, and water [5,6]. Thus, in addition to the recovery efficiency of useful substances, special attention should be paid to the pollution control effects of environmental contaminants during the treatment or disposal of PM [7–9].

The resource utilization approaches of PM mainly include biochemical technologies (such as composting and anaerobic digestion) and thermochemical technologies (such as liquefaction, pyrolysis, and incineration) [10–13]. Liquefaction is the process of converting organic materials into bio-oil through heating under the action of solvents (water or organic solvents) (temperature 250–400 °C, pressure 5–20 MPa) while producing two by-products: hydrochar and syngas [14,15]. An advantage of liquefaction technology is its ability to directly process high-humidity materials. The liquefaction of PM, a type of agricultural organic solid waste with high moisture content, has received widespread attention. Water, ethanol, and crude glycerol have been tested as solvents for the liquefaction of PM [16–19]. Moreover, the yield and quality of bio-oil obtained from the liquefaction of PM can be

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improved by introducing some other biomasses, such as sewage sludge, algae, and lignocellulose [20–23]. In a study by Cheng *et al.* [24,25], the refinement of bio-oil derived from the liquefaction of PM was explored.

Relatively little research has been conducted on the control effects of pollutants in the treatment of PM by liquefaction. The primary environmental issue associated with the treatment and disposal of PM was the pollution of heavy metals. Related studies have shown that most of the heavy metals in PM were transferred to solid products (hydrochar) after liquefaction treatment, and the proportion of active heavy metals was decreased, which meant the mitigation of the contamination degree/risk of heavy metals [26–28]. However, the pollution control effects of heavy metals during the co-liquefaction of PM with various biomass have not been systematically explored. Ali Shah *et al.* [20] studied the distribution of inorganic elements (including some heavy metals) during the co-liquefaction of PM and sewage sludge; however, no in-depth investigation was conducted on the changes in the form, activity, and pollution level/risk of heavy metals, which is crucial for understanding the pollution control effects of heavy metals. In addition, PM often contains a certain amount of polycyclic aromatic hydrocarbons (PAHs); therefore, the transformation effects of PAHs during PM treatment are also very important. Adánez-Rubio *et al.* [7] investigated the transformation behaviors of PAHs during the pyrolysis of PM. In a study by Lang *et al.* [29], the transformation behaviors of PAHs during the hydrothermal carbonization of PM were reported. However, the net synthesis of PAHs in the treatment of PM was neglected, which is essential for understanding the pollution control effects of PAHs. It is also important to note that the distribution, synthesis, and transformation of PAHs during the liquefaction of PM have not been reported.

Further clarification of the pollution control effects of heavy metals and PAHs during the treatment of PM by liquefaction can provide important support for the improvement of PM liquefaction technology. This study aimed to explore the migration/transformation characteristics of heavy metals and PAHs during the co-liquefaction treatment of PM and lignocellulose. Regarding heavy metals, not only were the changes in their contents discussed, but their chemical speciation, pollution levels, and environmental risks were also clarified. In addition to clarifying the changes in the content and toxicity of PAHs, the synthesis behaviors of PAHs were explored.

2. Materials and Methods

2.1. Materials

The collection and pre-treatment of raw biomass materials (PM, rice straw (RS), and wood sawdust (WS)) used in this study and their basic physicochemical properties have been presented in detail in a previous study [23]. HCl, HNO, H_2SO_4, $HClO_4$, HF, and Na_2SO_4 were all of analytical purity and obtained from Sinopharm Chemical Reagent Company (China). Organic reagents, such as ethanol, acetone, hexane, and methylene chloride, were of pesticide residue-grade purity and were provided by ANPEL Reagent Company Limited (Shanghai, China).

2.2. Co-liquefaction experiments

Co-liquefaction treatments of PM with either RS or WS were performed in an intermittent reactor (Parr 4576A, USA). The steps of the liquefaction reaction and product separation were based on a previous study [23]. In the present study, liquefaction products, which were selected to explore the pollution control effects of heavy metals and PAHs, were obtained under the optimized conditions (*i.e.*, 280 °C, 30 min, 0.1 $g \cdot ml^{-1}$ of solid–liquid ratio), and a mixture with an equal ratio of ethanol and water was used as a solvent. BO-PM-RS/WS and HC-PM-RS/WS represented the bio-oil (BO) and hydrochar (HC) products obtained from the co-treatment of PM with either RS or WS by liquefaction, respectively. To better reflect the influence of the introduction of lignocellulose, the liquefaction of pure PM was selected as the control group under the same optimized conditions, and the corresponding liquefaction products were also collected and tested for analysis.

2.3. Analysis of heavy metals

2.3.1. Total content of heavy metals

Multiple acid combination digestion methods were used to completely extract heavy metals from the feedstocks and their liquefaction products. The specific steps were as follows: (i) transfer 0.3 g of a test sample to a polytetrafluoroethylene beaker and add 5 ml of hydrochloric acid; (ii) heat the mixture to 120 °C and then sequentially add nitric acid (5 ml), hydrofluoric acid (5 ml), and perchloric acid (3 ml); (iii) further treat the mixture at 180 °C for 1 h; (iv) when the sample is digested to near dryness, add 1 ml of 1% HNO_3 to dissolve the final residue; (v) dilute the dissolved solution using deionized water and then filter it using a 0.45-μm filter membrane.

2.3.2. Chemical speciation of heavy metals

A classic sequential extraction method proposed by the European Community Bureau of Reference (BCR) was used to separate heavy metals into different forms. The specific steps are listed in detail in related studies [30–32]. According to this extraction method, four chemical species of heavy metals were identified, including acid-soluble/exchangeable speciation (S_1), reducible speciation (S_2), oxidizable speciation (S_3), and residual speciation (S_4). Among them, S_1 and S_2 are considered directly toxic/bioavailable forms, while S_3 and S_4 are classified as potentially toxic/bioavailable and non-toxic/stable forms, respectively [33].

2.3.3. Leachable content of heavy metals

An H_2SO_4–HNO_3 leaching agent was first prepared according to methods reported in Ref. [34] and then was used to separate the leachable heavy metals.

2.3.4. Detection of heavy metals

The specific amounts of heavy metals in the digestion, extraction, and leaching solutions were determined using a plasma emission spectrometer (NexION 1000, PerkinElmer, USA). Based on the abundance and toxicity of heavy metals in the samples, this study focused on six heavy metals, namely copper, zinc, cadmium, chromium, lead, and nickel.

2.4. Analysis of PAHs

2.4.1. Extraction of PAHs

To extract the total content of PAHs, acetone–hexane mixed solvents were used as leaching agents, while the extraction of leachable PAHs was performed using a mixture of H_2SO_4 and HNO_3 as leaching agents. The preparation of extraction solvents and the specific extraction operations can be found in the previous reports [35].

2.4.2. Purification of PAHs

All extraction solutions were purified using a dedicated silicone purification column for PAHs, provided by ANPEL Reagent Company Limited (SBEQ-CA1355-clean, CNW, Shanghai, China). The

detailed purification procedure is described in a previous study [35].

2.4.3. Detection of PAHs

Detection of PAHs was performed using gas chromatography-mass spectrometry. A dedicated chromatographic column for detecting PAHs was obtained from ANPEL Reagent Company Limited (CD-5MS). The selected ion monitoring mode was used to perform the qualitative analysis of the PAHs, with the aid of an Agilent gas chromatography-mass spectrometer (GC-MS, 7890B-5977A Agilent, USA). Based on the calibration curves for 16 priority-controlled PAHs, a quantitative analysis of the PAHs was performed. The properties and the calibration curves of the 16 priority-controlled PAHs are listed in Table S1 in Supplementary Material.

2.5. Evaluation methods for environmental toxicity and risk

2.5.1. Contamination degree/risk of heavy metals

To more accurately evaluate the pollution control effects of heavy metals during liquefaction, this study adopted two pollution degree/risk assessment methods based on the contents of heavy metals distributed in different chemical species: the global contamination factor (GCF) and global risk index (GRI) (Eqs. (1) and (2)). The classification criteria for the pollution level or risk of heavy metals are listed in Table S2 [36,37].

$$\mathrm{GCF} = \sum_{i=1}^{n} \mathrm{ICF}_i = \sum_{i=1}^{n} \left(\frac{C_{S1} + C_{S2} + C_{S3}}{C_{S4}} \right)_i \tag{1}$$

$$\mathrm{GRI} = \sum_{i=1}^{n} \mathrm{TF}_i \mathrm{ICF}_i \tag{2}$$

where ICF_i (individual contamination factor) is the pollution level of a single metal (i); C_{S1}, C_{S2}, C_{S3}, and C_{S4} are the contents of acid-soluble/exchangeable speciation (S_1), reducible speciation (S_2), oxidizable speciation (S_3), and residual speciation (S_4), respectively; TF_i is the toxic factor of a single metal (i).

2.5.2. Ecological toxicity of PAHs

The toxicity equivalent method was used to evaluate the ecological toxicity of the PAHs (Eq. (3)) [38,39].

$$\mathrm{TEQ} = \sum_{i=1}^{n} \mathrm{TEQ}_i = \sum_{i=1}^{n} \mathrm{TEF}_i C_i \tag{3}$$

where TEQ_i is the toxicity equivalent value of a single PAH; C_i is the total content of a single PAH; TEF_i is the toxic equivalent factor relative to the toxicity of BaP (Table S1).

2.6. Statistical analysis

To ensure the accuracy of the experimental data, each processed sample contains three parallel samples, and the reported data are the average and standard error of the three parallel samples.

3. Results and Discussion

3.1. Concentrations and forms of heavy metals

3.1.1. Total content and distribution of heavy metals

The total concentrations of heavy metals in the feedstocks (PM, WS, and RS) and liquefaction products (bio-oil and hydrochar) are shown in Figs. 1 and 2. Compared with the lignocellulosic biomass (WS and RS), PM contained much higher contents of Cu and Zn (570.3 $\mathrm{mg \cdot kg^{-1}}$ and 634.1 $\mathrm{mg \cdot kg^{-1}}$, respectively). This was primarily because Cu and Zn are often used as feed additives to promote pig growth. However, these heavy metals are less absorbed by animals, and most are excreted from the body through feces and urine [27,28]. The contents of the other four metals (Cr, Ni, Cd, and Pb) in the three biomass materials were relatively low, especially that of Cd, which was present only at trace levels (0.16–0.31 $\mathrm{mg \cdot kg^{-1}}$). Notably, after liquefaction, heavy metals were concentrated in the hydrochars (solid product), and a small portion (lower than 13%) migrated into the bio-oil (liquid product) (Fig. 2). Similar results were also reported in the liquefaction of heavy-metal-enriched or polluted biomass [40,41]. The low entry of heavy metals into the bio-oil products (organic phase) could be attributed to the dominance of heavy metals in inorganic forms in the raw materials. Additionally, during liquefaction, the degradation probability of organic compounds containing heavy metals often exceeds the combination probability of heavy metals with organic compounds [42].

The enrichment of heavy metals in the hydrochars could be attributed to the following three factors: (i) the developed pore structure and organic framework of hydrochar reabsorbed and re-fixed most of the heavy metals; (ii) the degradation and transformation of organic matter indirectly increased the content of heavy metals in the hydrochar; (iii) the introduction of WS/RS in the treatment of PM by liquefaction led to a decreased hydrochar yield, which improved the content of heavy metals in the hydrochar for the cases of Cr, Ni, and Cd [40,43,44]. However, the HC-PM-WS/RS contained similar concentrations of Cu and Zn as HC-PM (Fig. 1(a) and (d)), which was attributed to the much lower contents of Cu and Zn in WS/RS than in PM. According to the standard for biochar used in soil issued by the International Biochar Initiative (IBI, IBI-STD-2.1), all six heavy metals in the hydrochars complied with the range of the maximum allowed thresholds (as listed in Fig. 1).

The contents of copper, zinc, chromium, and nickel in the bio-oil products were in the ranges of 2.0–6.0 $\mathrm{mg \cdot kg^{-1}}$, 0–3 $\mathrm{mg \cdot kg^{-1}}$, 1.0–8.0 $\mathrm{mg \cdot kg^{-1}}$, and 0–19 $\mathrm{mg \cdot kg^{-1}}$, respectively, while cadmium and lead were not detected. During liquefaction, some heavy metal fragments may be decomposed and fused with bio-oil products [20,40]. The existing diesel and gasoline standards in China do not specify the content standards for heavy metals. However, it is evident that the higher the content of heavy metals, the greater the potential to cause environmental pollution during the use of gasoline or diesel. As shown in Fig. 2, some researchers have determined the amounts of heavy metals in conventional commercial diesel, and it is evident that copper, zinc, chromium, and nickel all exist at trace levels [30]. The presence of heavy metals in bio-oil may be undesirable when the bio-oil is used as fuel, and it may also lead to a deactivation of catalyst in the relevant upgrading processes [26].

3.1.2. Chemical speciation of heavy metals

Fig. 3 depicts the chemical speciation of heavy metals in the raw feedstocks and hydrochars. Except for Cr and Pb, the percentages of directly toxic/bioavailable Cu, Cd, Ni and Zn (S_1 and S_2) in the raw PM were all greater than 50%. Considering the high abundance of heavy metals (especially Cu and Zn) in PM, the long-term direct use of untreated PM will inevitably pose huge environmental pollution risks. In the two lignocellulosic biomasses (WS and RS), some heavy metals (*e.g.,* Zn, Ni, and Cd) had a high proportion of active forms. However, in general, it is unnecessary to consider the heavy metal hazards that WS and RS may pose to the environment, considering their low total content of heavy metals.

After the liquefaction treatment, the proportions of potentially bioavailable/stable heavy metals (S_3 and S_4) in the hydrochars were significantly promoted. In other words, the liquefaction treatment

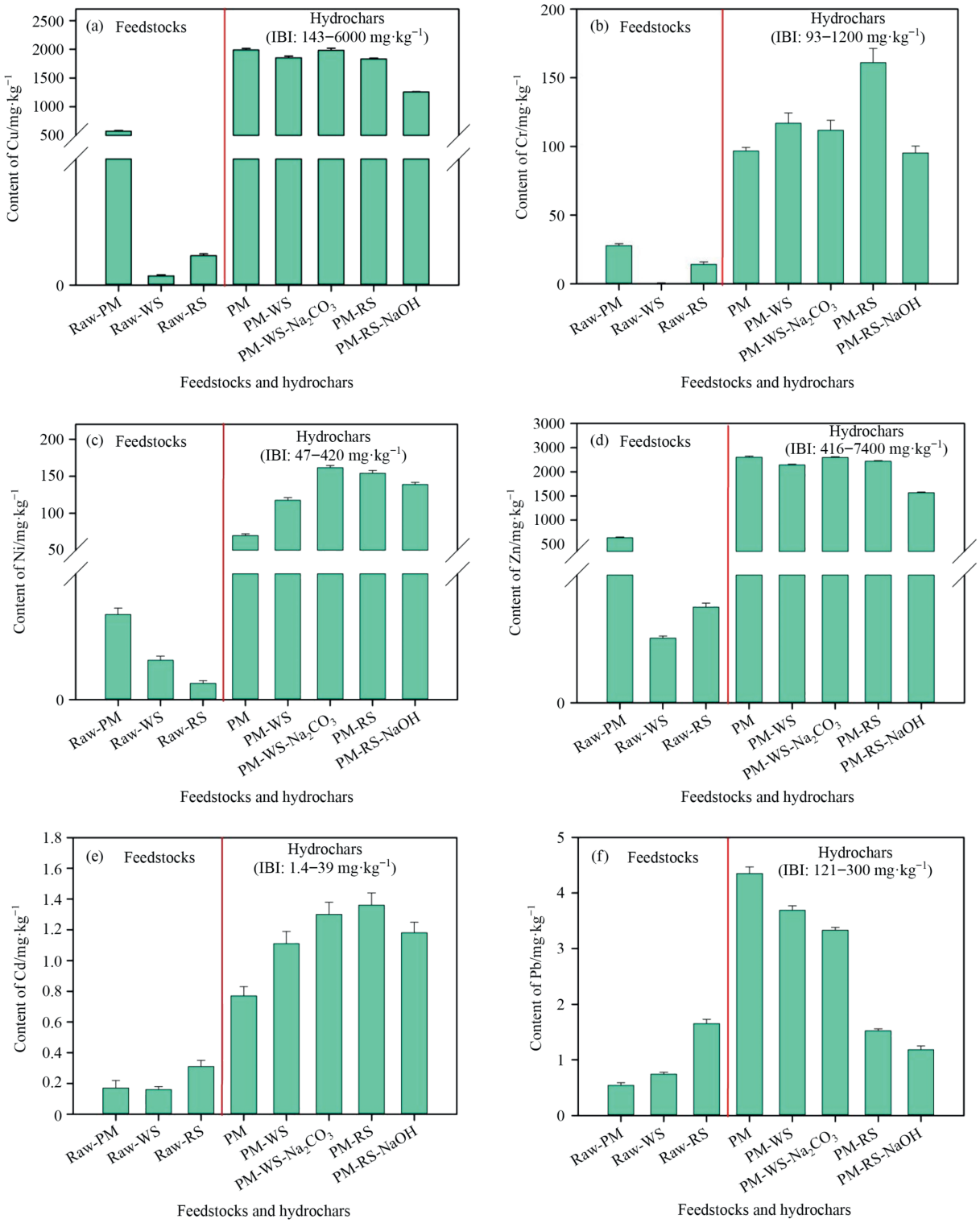

Fig. 1. Total contents of heavy metals in feedstocks and hydrochars: (a) Cu, (b) Cr, (c) Ni, (d) Zn, (d) Cd, (f) Pb.

enhanced the transformation of the directly toxic/bioavailable heavy metals (S_1 and S_2) into potentially bioavailable/stable forms (S_3 and S_4). 23.9% to 62.0% of the Cu in feedstocks was bound to the directly toxic/bioavailable forms (S_1 and S_2), and it was reduced to less than 2%. The increase in the proportion of oxidized copper was particularly significant, from 24.8% to 35.1% in the feedstocks to 76.1% to 88.6% in the hydrochars. A similar phenomenon was observed for Zn and Cd. The reason for this phenomenon might be the preference for Cu, Zn, and Cd bound to organic complexes during liquefaction [28]. In particular, directly toxic/bioavailable heavy metals (S_1 and S_2) were prone to first dissolve into the liquid phase and then combine with rich oxides, oxygen-containing

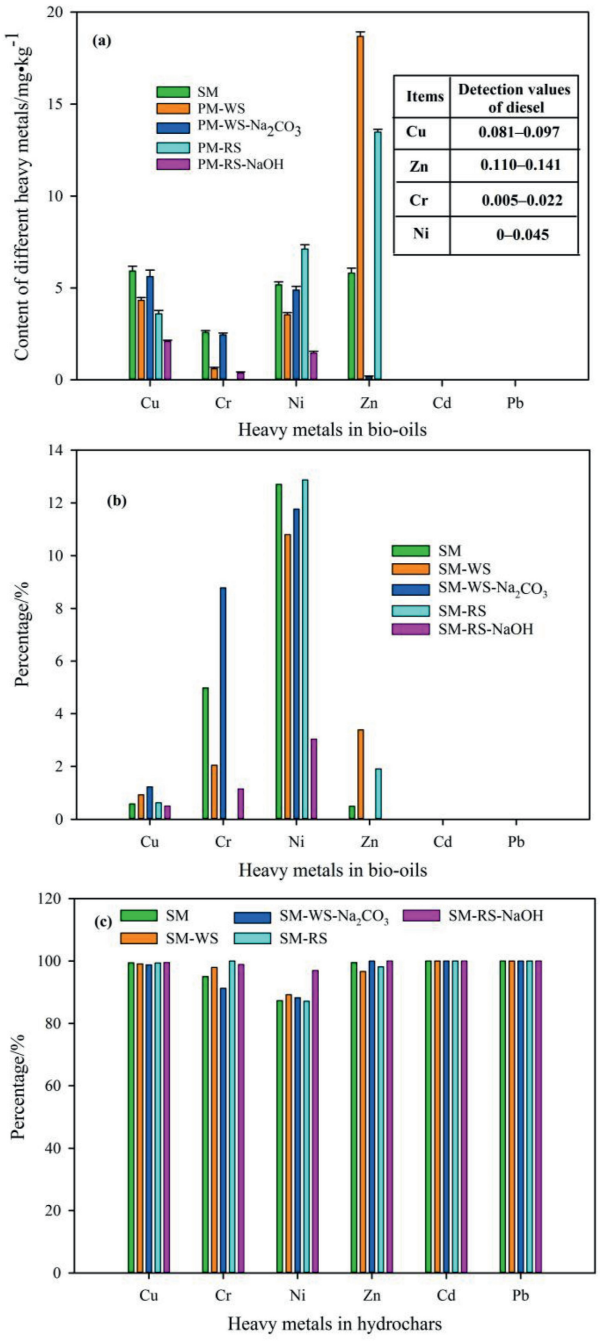

Fig. 2. Total contents of heavy metals in bio-oils and distributions of heavy metals in liquefaction products: (a) total contents of heavy metals in bio-oils, (b) distribution's in bio-oil, (c) distribution's in hydrochars.

functional groups, and organic ligands produced during liquefaction, finally transforming into potentially bioavailable/stable forms (S_3 and S_4) [43].

The percentage of Cr present in the acid-soluble, exchangeable, and reducible forms in the feedstocks was below 3%, and the residual Cr (S_4) accounted for the majority (over 87%). The liquefaction treatment further strengthened this trend, reducing the directly toxic/bioavailable Cr to approximately 1%, and even partially converting the oxidized Cr into residual speciation. The residual Pb in the feedstocks accounted for 42.3% to 62.6%, which was promoted to over 91% in the hydrochars. Meanwhile, the proportions of Pb in other forms (S_1, S_2, and S_3) were reduced, especially for the oxidizable Pb. Heavy metals bound to organic matter (S_3) can also be released with the degradation of organic matter, which then would combine with some inorganic components such as silicates, SiO_2, Al_2O_3, and sulfides, and finally transform into stable heavy metals (S_4) [43]. The percentages of Ni belonging to S_1 and S_2 in the hydrochars were still relatively high, ranging from 24.9% to 42.4%, although the oxidizable and residual Ni (S_3 and S_4) were increased.

In summary, the transformation of active heavy metals into stable forms during the co-treatment of PM-WS/RS by liquefaction could be understood from multiple perspectives (Fig. 4). Most active heavy metals in liquefaction feedstocks were re-released during hydrothermal treatment, and then became more stable through processes such as adsorption, precipitation, and complexation. Compared with liquefaction feedstocks, the hydrochars had a certain pore structure and, thus, a stronger adsorption capacity for heavy metal ions, which could passivate heavy metals to a certain extent. Some inorganic anionic groups present in raw biomass may further combine with metal ions to form stable heavy-metal salt precipitates such as silicates, sulfates, and carbonate. Moreover, some organic compounds with special functional groups, formed during the co-liquefaction process, can combine with metal ions, resulting in the formation of stable organic–metal-salt precipitates [27,40,41,44].

3.1.3. Leachable concentrations of heavy metals

Table 1 lists the leachable content of heavy metals in the raw PM and hydrochar products, which represents the leaching toxicity of the hazardous components of solid waste and its reused materials under acidic precipitation conditions during land use. The leaching rate of heavy metals has been confirmed to correlate strongly with the proportion of S_1 [30]. As shown in Fig. 3, the percentages of Cu, Ni, Zn, and Cd bound to S_1 in the feedstocks ranged from 11.40% to 51.68%, and they were significantly reduced in the hydrochars except for that of Ni. For Pb and Cr, the proportions of S_1 in the feedstocks and hydrochars were both below 5%. As expected, leachable Pb and Cr were not detected in the feedstocks/hydrochars, whereas leachable Cu, Ni, Zn, and Cd were detected. Notably, the leaching ability of Cu, Ni, Zn, and Cd in hydrochars was mitigated on the whole. In particular, the contents of leachable Cd in the WS and RS were 0.56 and 5.23 $\mu g \cdot L^{-1}$, respectively. However, leachable Cd was not detected in the hydrochar products (Table 1). Liquefaction treatment can immobilize heavy metals in feedstocks by changing the form of heavy metals *via* adsorption, complexation, and precipitation, resulting in a lower leaching risk of heavy metals in hydrochars [40,45]. In addition, compared to the WS, introducing RS during the liquefaction of PM was more conducive to alleviating the leaching toxicity of heavy metals in the hydrochars. Furthermore, the use of catalysts further reduced the leachable content of heavy metals in the hydrochars.

3.2. Pollution control effect of heavy metals

Fig. 5 shows the pollution control effects of heavy metals in the co-treatment of PM-WS/RS by liquefaction. As shown in Fig. 5(a), the contamination of heavy metals in PM reached a high level, which was mainly caused by Cu and Zn. As expected, the hydrochars exhibited lower levels of heavy metal contamination. Particularly, for the co-treatment of PM with RS by liquefaction, the contamination level of heavy metals in the hydrochar was reduced to a moderate level, mainly due to an alleviation in the Cu and Zn pollution levels. The degree of Cu and Zn pollution decreased from high levels in the raw PM to considerable and moderate levels in

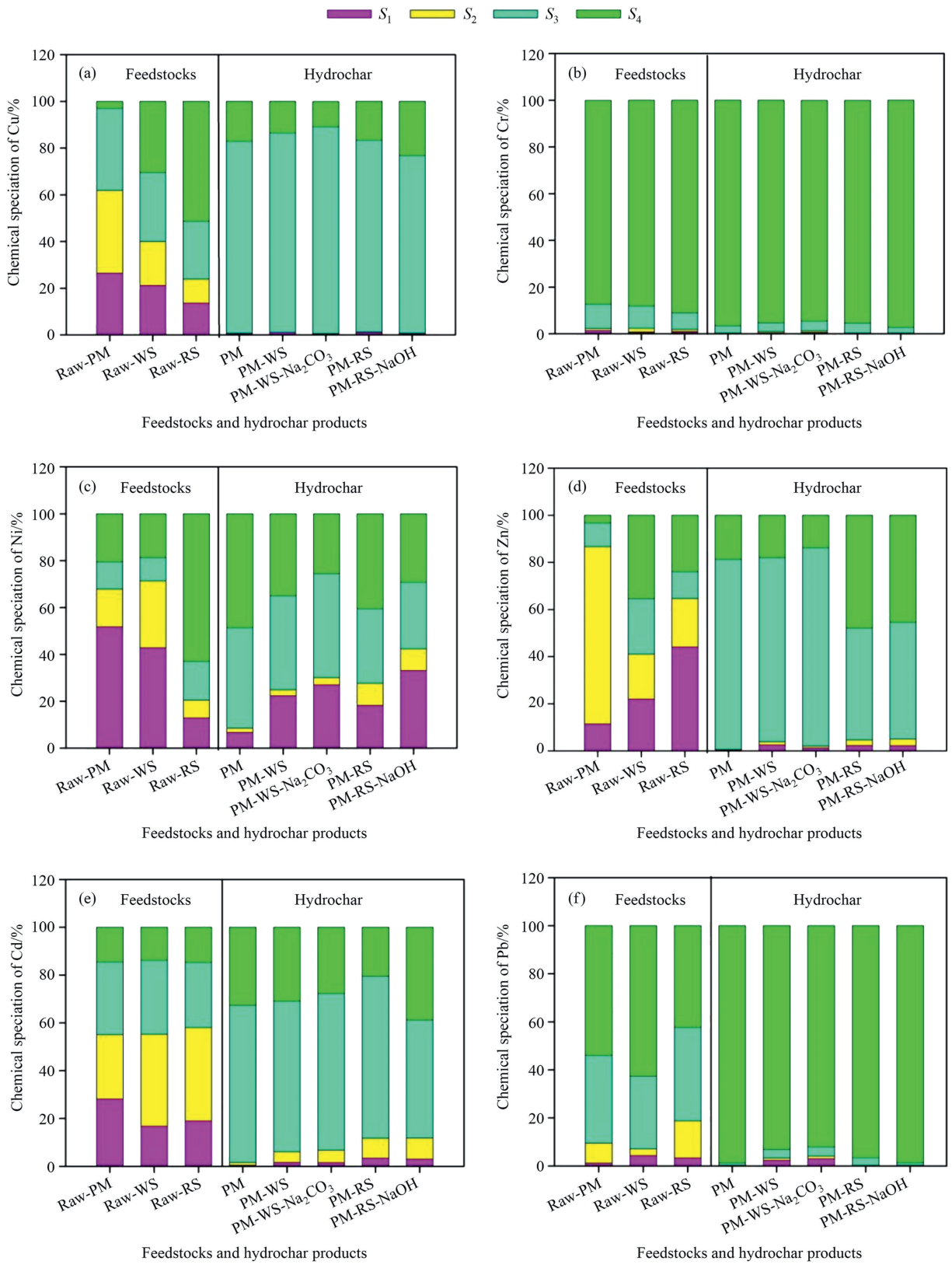

Fig. 3. Chemical speciation of heavy metals in feedstocks and hydrochar: (a) Cu, (b) Cr, (c) Ni, (d) Zn, (d) Cd, (f) Pb.

the hydrochars, respectively. According to the GRI results in Fig. 5(b), the raw PM posed a considerable risk to the ecological environment, mainly due to the high ecological risks of Cu and Cd. Surprisingly, the ecological risk of heavy metals in the hydrochars decreased to a low level. In conclusion, liquefaction treatment demonstrated immobilization effects on heavy metals in raw

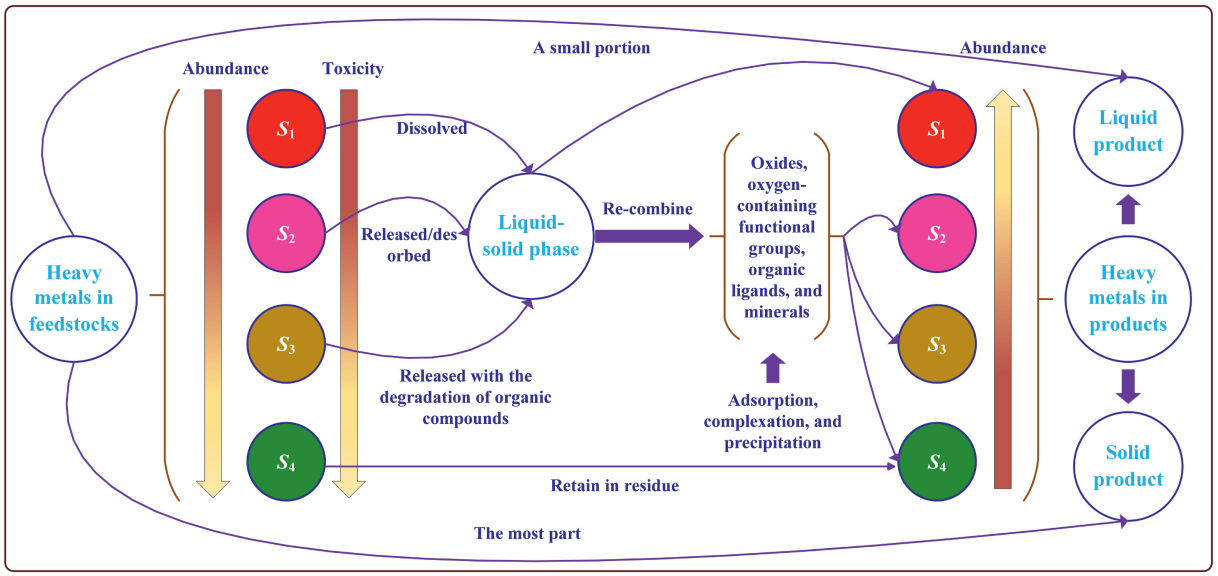

Fig. 4. Transformation pathways of heavy metals in liquefaction treatment.

biomass materials, thereby reducing the pollution degree and risk of heavy metals. When NaOH was added as a catalyst in the co-liquefaction treatment of PM with RS, the pollution control effects of the heavy metals were optimal.

3.3. Concentrations and forms of PAHs

3.3.1. Total content and distribution of PAHs

Table 2 presents the content, toxicity equivalent, and forms of PAHs in the PM feedstock. The total contents, forms, and distributions of the PAHs in the bio-oil and hydrochars are shown in Fig. 6. As listed in Table, the total amounts of PAHs in the PM feedstock reached 3.73 $mg \cdot kg^{-1}$, which was slightly lower than that (5.44 $mg \cdot kg^{-1}$) reported by Lang *et al* [29].

The most abundant PAHs in the raw PM were Pyr (1.47 $mg \cdot kg^{-1}$), followed by Ant (0.57 $mg \cdot kg^{-1}$) and IcP (0.39 $mg \cdot kg^{-1}$). The PAHs in the raw PM were dominated by four-ring PAHs (1.74 $mg \cdot kg^{-1}$) and three-ring PAHs (0.97 $mg \cdot kg^{-1}$); thus the percentage of middle-molecular-weight (MMW, four-ring) PAHs reached 46.68%. The main sources of PAHs in the PM include two aspects: firstly, the atmospheric deposition of PAHs with solid particles during PM stacking; secondly, pigs are exposed to PAHs, and the unabsorbed or metabolized PAHs are excreted through urine or feces. The main route of exposure for pigs is the digestive tract (ingestion of feed contaminated with PAHs), followed by respiration and skin contact with PAHs present in the air. PAHs in feed mainly originate from the raw materials (crops) used in feed preparation, which come into contact with PAHs in the atmospheric environment through atmospheric solid deposition (attachment of PAHs) and respiration during growth. Additionally, PAHs are also ingested by crops from soil and water bodies [7,46–48].

As depicted in Fig. 6(a), the total concentrations of PAHs in the hydrochar produced from the liquefaction of pure PM was 3.53 $mg \cdot kg^{-1}$, which was close to that in raw PM, whereas it was reduced by the introduction of lignocellulose (WS and RS). The total concentrations of PAHs in hydrochar produced from the co-treatment of PM-WS by liquefaction was 2.45 $mg \cdot kg^{-1}$, which was further reduced to 1.76 $mg \cdot kg^{-1}$ following the addition of Na_2CO_3 as a catalyst. Regarding the co-treatment of PM-RS by liquefaction, the total content of PAHs in the hydrochar was 1.77 $mg \cdot kg^{-1}$, while it was slightly increased to 2.45 $mg \cdot kg^{-1}$ when NaOH was used as a catalyst. As reported in the literature, the introduction of WS/RS in the treatment of PM by liquefaction reduced the specific surface area and pore volume of the hydrochars [23]. The weakened adsorption ability of hydrochar might have been an important reason for the decrease in the total

Table 1
Leachable content of heavy metals in feedstocks and hydrochars.

Items	Heavy metals × 10^3/$mg \cdot L^{-1}$					
	Cu	Cr	Ni	Zn	Cd	Pb
PM	35510.83 ± 827.59	– ①	631.60 ± 15.13	811.94 ± 19.69	–	–
WS	26.83 ± 4.00	–	72.75 ± 13.11	77.44 ± 10.15	0.56 ± 0.20	–
RS	195.48 ± 18.34	–	63.49 ± 7.81	2976.41 ± 29.82	5.23 ± 0.81	–
HC-PM	475.16 ± 26.53	–	161.50 ± 18.69	–	–	–
HC-PM-WS	509.82 ± 23.59	–	537.03 ± 20.08	385.17 ± 21.64	–	–
HC-PM-WS-Na_2CO_3	171.56 ± 9.64	–	277.52 ± 24.98	–	–	–
HC-PM-RS	135.81 ± 13.52	–	163.82 ± 12.53	98.11 ± 14.42	–	–
HC-PM-RS-NaOH	39.80 ± 7.21	–	73.88 ± 10.54	–	–	–
Standard value②/$mg \cdot L^{-1}$	100	15	5.0	100	1.0	5.0

① Undetected.
② Identification standards for hazardous wastes.

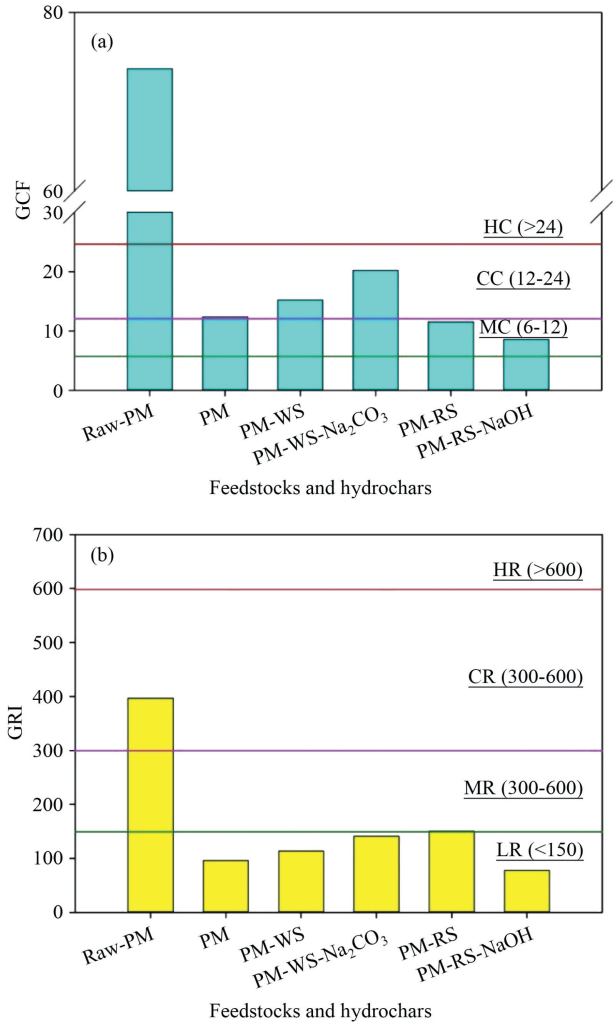

Fig. 5. GCF and GRI values of heavy metals in feedstocks and hydrochar: (a) GCF values, (b) GRI values.

concentrations of PAHs in the hydrochars derived from the co-liquefaction treatment. It was also found that the addition of WS and RS promoted the transformation of low-molecular-weight (LMW, two- and three-ring) PAHs to high-molecular-weight (HMW, five- and six-ring) PAHs, whereas the introduction of NaOH resulted in the opposite trend (Fig. 6(c)). The IBI and the European Biochar Foundation (EBF) issued the limits for PAHs in biochar samples [7,49]. All hydrochars produced in the co-liquefaction treatment of PM-WS/RS met the recommendation for premium-grade biochar (4 $mg \cdot kg^{-1}$).

Unlike hydrochars, the total concentrations of PAHs in the bio-oil products reached 57.32–132.33 $mg \cdot kg^{-1}$ (Fig. 6(b)). The introduction of lignocellulose, especially for WS, promoted the total concentrations of PAHs in bio-oil. Interestingly, the use of catalysts reduced the content of PAHs in bio-oil products. In particular, the bio-oil produced during the co-liquefaction of PM-RS with NaOH as the catalyst contained the lowest concentrations of PAHs (57.32 $mg \cdot kg^{-1}$). In addition, co-liquefaction treatment enhanced the transformation of HMW-PAHs to LMW/MMW-PAHs in the bio-oil (Fig. 6(d)).

The distribution characteristics of the PAHs in the liquefaction products were determined by combining the yields of the biochar and bio-oil products with the contents of PAHs (Fig. 6(e), (f)). Most of the PAHs were migrated into the bio-oil products, beyond 97%. Notably, co-liquefaction treatment enhanced the transfer of PAHs from the hydrochars to the bio-oil products. A similar phenomenon was reported for the liquefaction of sewage sludge, in which more than 89% of PAHs were distributed in bio-oils [35]. Thus far, there is no relevant standard or specification for the limit values of PAHs in bio-oil. When bio-oil is used for subsequent practical applications, the environmental hazards and health risks posed by PAHs in bio-oil must be further clarified.

3.3.2. *Synthesis behavior of PAHs*

Unlike heavy metals, PAHs can be synthesized during the processing and transformation of any organic compound, and understanding their formation is crucial [50]. Assuming that the content of PAHs in two lignocellulosic materials (WS/RS) was negligible, the net synthesis amount of PAHs was obtained by subtracting the actual content of PAHs in PM from the relative content of PAHs in the liquefaction products (actual content multiplied by the yield of the liquefaction products).

Fig. 7(a) depicts the net amount of PAHs synthesized during the co-liquefaction treatment of PM-WS/RS. The net amount of PAHs synthesized in the liquefaction of pure PM was 30.96 $mg \cdot kg^{-1}$. The introduction of RS and WS increased the net synthesis of PAHs to 40.48 $mg \cdot kg^{-1}$ and 73.98 $mg \cdot kg^{-1}$,

Table 2
Content, toxicity equivalent, and forms of PAHs in raw PM.

PAHs	Total content $\times 10^3$/mg·kg^{-1}	TEQ $\times 10^3$/mg·kg^{-1}	Ring number	Content $\times 10^3$/mg·kg^{-1}	Molecular	Percentage/%	Leachable content $\times 10^3$/mg·kg^{-1}
Nap	147.31 ± 15.85	0.147	2	0.1473	LMW	29.89	60.15 ± 3.97
Acy	41.56 ± 4.22	0.042	3	0.9664			12.22 ± 1.79
Ace	55.32 ± 3.14	0.055					21.88 ± 2.71
Flu	78.53 ± 3.54	0.079					36.28 ± 3.62
Phe	221.70 ± 7.57	0.222					62.60 ± 3.32
Ant	569.25 ± 10.93	5.692					27.21 ± 2.00
Fla	90.91 ± 6.14	0.091	4	1.7395	MMW	46.68	20.57 ± 1.86
Pyr	147.27 ± 41.09	1.473					14.80 ± 1.77
BaA	130.33 ± 3.84	13.033					24.48 ± 2.25
Chr	45.03 ± 3.41	0.450					10.22 ± 0.75
BbF	74.43 ± 4.71	7.443	5	0.3410	HMW	23.43	19.65 ± 2.32
BkF	88.87 ± 5.84	8.887					22.45 ± 1.80
BaP	92.45 ± 5.29	92.452					26.86 ± 2.83
DaA	85.26 ± 5.64	85.261					–①
IcP	387.56 ± 10.06	38.756	6	0.5320			23.88 ± 2.55
BgP	144.44 ± 7.02	1.444					–
Σ	3726.23	255.527	–	3.7262	–	100.00	383.24

① Undetected.

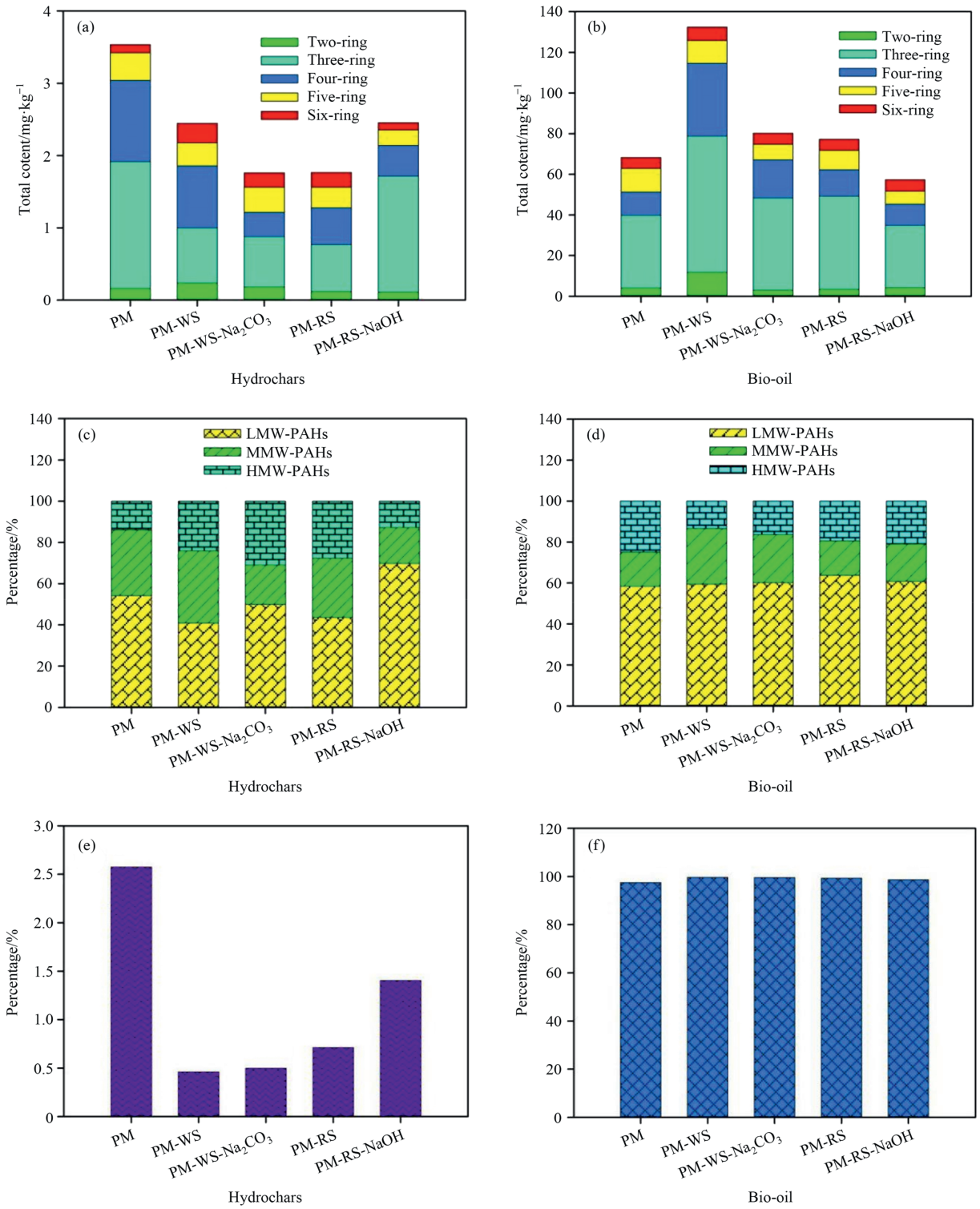

Fig. 6. Total contents, forms, and distributions of PAHs in bio-oil and hydrochars: (a) total contents in hydrochars, (b) total contents in bio-oil, (c) forms in hydrochars, (d) forms in bio-oil, (d) distributions in hydrochars, (f) distributions in bio-oil.

respectively. This indicated that the introduction of both RS and WS promoted the formation of PAHs. The specific reason for this phenomenon may be that the formation of benzene and phenolic compounds (important PAH precursors) was improved with the increase of lignin components in the liquefaction feedstocks [23,35,51–53]. Interestingly, the net synthesis of PAHs was reduced to 29.65 mg·kg^{-1} (PM-RS-NaOH) and 47.57 mg·kg^{-1} (PM-WS-Na_2CO_3), when catalysts were added during the co-liquefaction of PM-WS/RS. Therefore, the alkaline catalysts were beneficial for reducing the synthesis of PAHs during liquefaction. It has been speculated that the addition of alkali metal catalysts increased the pH of the entire liquefaction system, which can represent the synthesis of PAHs [38]. Similar results were reported for the hydrothermal gasification of sewage sludge, where there

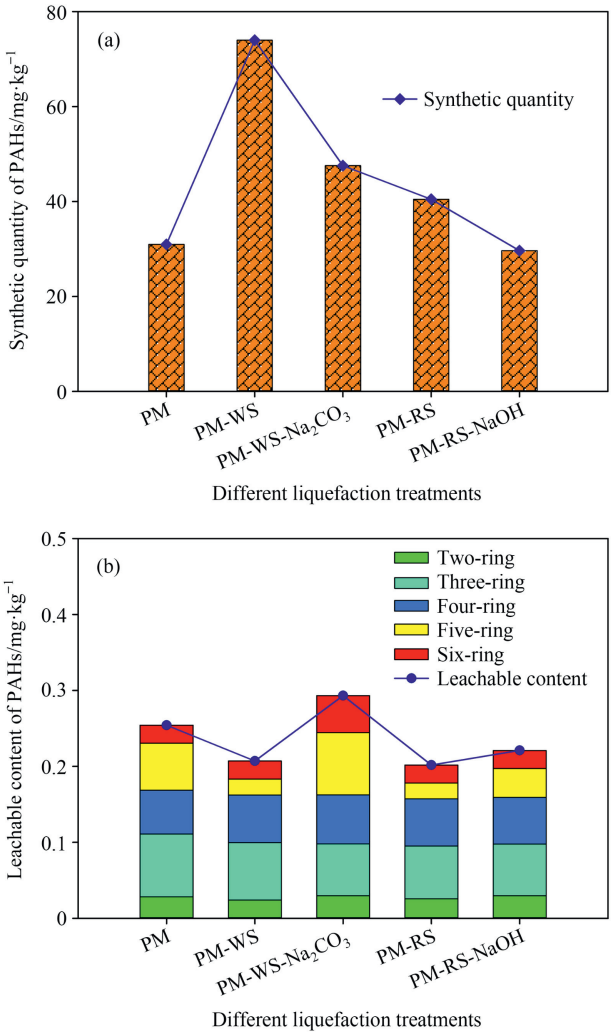

Fig. 7. Synthetic behaviors of PAHs during co-liquefaction treatment and leachable content of PAHs in hydrochars: (a) synthesis amount, (b) leachable content.

was a negative correlation between the net synthesis of PAHs and the pH of sewage sludge [54]. The development of porous properties of hydrochar might also enhance the adsorption of PAHs, thus alleviating the leaching of PAHs [38].

Fig. 8 demonstrates the preliminary transformation pathways of PAHs during the liquefaction treatment. Compared to that of heavy metals, the transformation pathway of PAHs was more complex, considering that the re-synthesis of PAHs also occurred during the degradation process of organic matter. The identified pathways for the formation of PAHs included six aspects: (i) from alkenes and dienes *via* the Diels–Alder mechanism; (ii) from light aromatic compounds *via* the hydrogen abstraction-acetylene addition (HACA) mechanism; (iii) from phenolic compounds *via* the deoxygenation reaction; (iv) from alicyclic compounds *via* the aromatization reaction; (v) from phenyl radical *via* cyclopentadienyl recombination; (vi) from the mutual transformation of different molecular PAHs *via* the naphthalene zigzag reaction or decomposition reaction [29,38,52,53,55].

3.3.3. Leaching content of PAHs

Fig. 7(b) illustrates the amounts of leachable PAHs in the hydrochars. The amount of leachable PAHs in the PM feedstock was 0.38 $mg \cdot kg^{-1}$, and nearly half of the content comprised three-ring PAHs (Table 2). All hydrochars had a lower leaching content than that of raw PM, ranging from 0.21 $mg \cdot kg^{-1}$ to 0.29 $mg \cdot kg^{-1}$. The leaching content of PAHs in PM-derived hydrochar was 0.26 $mg \cdot kg^{-1}$, which was further reduced when RS/WS was introduced during the liquefaction of PM. However, the use of catalysts (NaOH and Na_2CO_3) slightly promoted the leaching content of PAHs in the hydrochars during the co-treatment of PM-RS/WS by liquefaction. In addition, all hydrochars exhibited similar leaching levels of two-, three- and four-ring PAHs, with some differences among those of five- and six-ring PAHs. Compared to raw PM, the hydrochars possessed a higher carbonization degree and a lower polarity, as indicated by the decrease in the O/C and (N + O)/C molar ratios [23]. The increase in carbonization degree meant a decrease in the amount of soluble organic matter, which was considered an important carrier for the leaching of PAHs [51,56]. The lower polarity of the hydrochars meant that the surface of the hydrochars had fewer polar functional groups and became more hydrophobic, which promoted the PAH–hydrochar interactions [35]. In a study on the freely dissolved PAHs in sewage sludge and its derived pyrolysis biochar, significant positive corrections were also found between the O/C and (N + O)/C molar ratios and the content of freely dissolved PAHs [57].

3.4. Pollution control effects of PAHs

The TEQ values of the PAHs in the different hydrochar and bio-oil products are depicted in Fig. 9. TEQ values reflect the

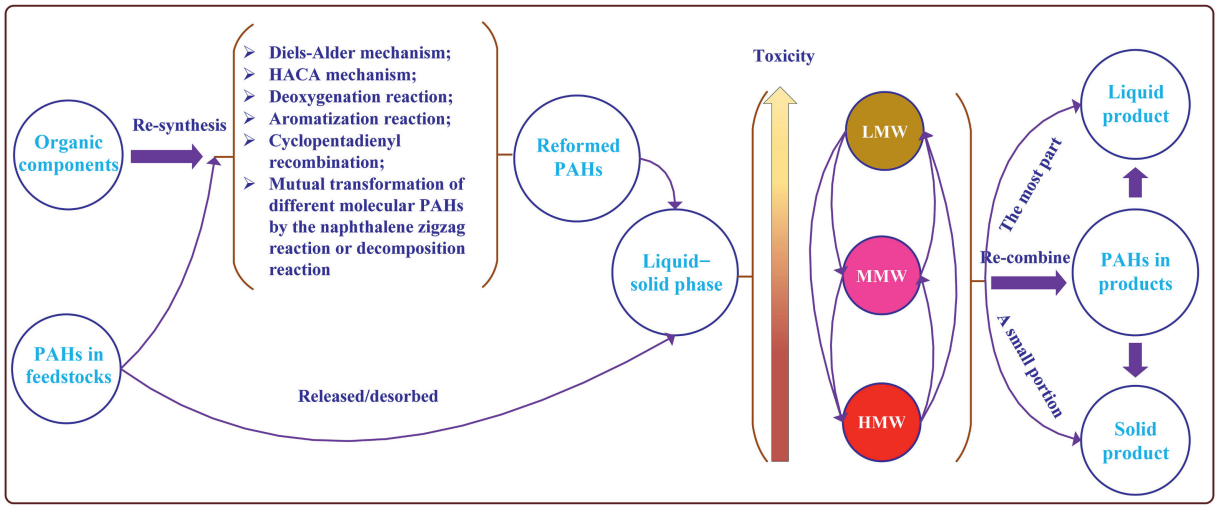

Fig. 8. Transformation pathways of PAHs in liquefaction treatment.

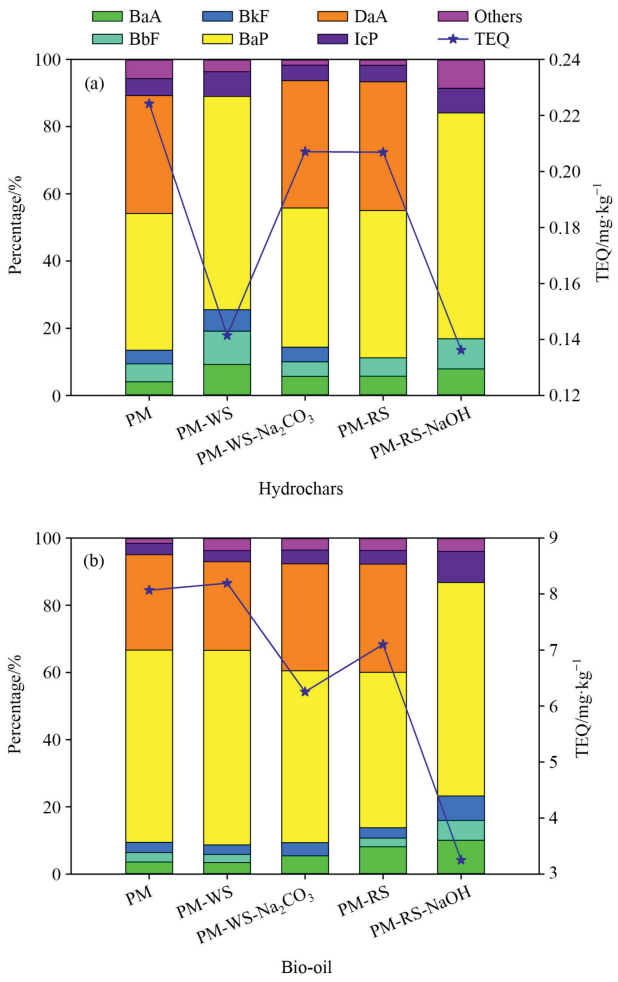

Fig. 9. *TEQ* of PAHs in hydrochar and bio-oil products: (a) hydrochars, (b) bio-oil.

carcinogenic risk of PAHs, and the lower the value, the more preferable. The PM feedstock had a TEQ value of 0.26 mg·kg^{-1}, and the contribution rate of BaP and DaA reached 69.5% (Table 2). Notably, TEQ values of the PAHs in hydrochars ranged from 0.14 mg·kg^{-1} to 0.22 mg·kg^{-1}. A recommended limit of 3.0 mg·kg^{-1} was proposed by the IBI [7]. Thus, all the hydrochars and raw PM satisfied this specification. Interestingly, the co-treatment of PM-WS/RS by liquefaction reduced the TEQ value of the PAHs in the hydrochars to some extent. Generally, PAHs with higher molecular weights exhibit stronger toxicity [38,58]. The hydrochar obtained from the co-liquefaction of PM-RS with NaOH as the catalyst contained the lowest percentage of HMW-PAHs, resulting in the lowest TEQ value of PAHs in the hydrochar.

The bio-oil products possessed higher TEQ values than hydrochar products, ranging from 3.3 mg·kg^{-1} to 8.2 mg·kg^{-1}, owing to the high concentrations of PAHs in bio-oils. The TEQ value of PAHs in the PM-derived bio-oil reached 8.07 mg·kg^{-1}, dominated by BaP and DaA (approximately 85%). The co-treatment of PM-WS by liquefaction resulted in a similar result for the TEQ value of PAHs in bio-oil. On the contrary, the co-treatment of PM-RS by liquefaction efficiently reduced the concentrations of BaP in the bio-oil (from 4.62 mg·kg^{-1} to 3.28 mg·kg^{-1}), which resulted in the TEQ value being lowered to 7.10 mg·kg^{-1}. The addition of alkaline catalysts was beneficial for reducing the content of PAHs (Fig. 9 (b)), leading to a reduction in the TEQ value. The use of Na_2CO_3 in the co-treatment of PM-WS by liquefaction reduced the content of BaP and DaA, resulting in a lower TEQ value of 6.25 mg·kg^{-1} in bio-oil. Notably, the use of NaOH in the co-liquefaction of PM-RS suppressed the formation of DaA, and the content of BaP was further reduced. Consequently, the TEQ of PAHs in the bio-oil was reduced to 3.25 mg·kg^{-1}. In summary, the co-treatment of PM-RS by liquefaction may be beneficial for the control of the toxicity of PAHs in the bio-oil. The use of alkaline catalysts (Na_2CO_3 and NaOH) may also be a feasible method to reduce the TEQ of PAHs.

4. Conclusions

Liquefaction treatment had a significant passivation effect on heavy metals, and the majority of heavy metals were transported into the biochar after liquefaction. Although the hydrochar possessed a higher content of heavy metals, the contamination degree/risk and leaching toxicity of the heavy metals in the hydrochar were mitigated. During the liquefaction process, the synthesis of PAHs could not be ignored, and the PAHs were distributed mainly in the bio-oil products. The presence of PAHs in hydrochar did not limit its application. Meanwhile, the introduction of lignocellulosic biomass further enhanced the pollution control effects of the liquefaction treatment of PM. Overall, compared to the WS, the RS exhibited better pollution control effects. Sufficient attention should be paid to the potential impacts of heavy metals and PAHs in the bio-oils. Further research is required to determine the content standards and actual effects of pollutants in bio-oil.

CRediT Authorship Contribution Statement

Zimin Luo: Writing – original draft, Investigation. Xinyi Huang: Writing – review & editing, Conceptualization. Chunfei Zhou: Methodology, Formal analysis. Min Jiang: Validation, Project administration. Xiaoping Liu: Supervision, Software. Huajun Huang: Writing – review & editing, Funding acquisition.

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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Supplementary Material

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