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Improvement of wheat (*T. aestivum*) straw catalytic fast pyrolysis for valuable chemicals production by coupling pretreatment of acid washing and torrefaction

Xiong Gao [a], Zhen Zhou [a], Brad Coward [b], Jiawei Wang [b,c], Hong Tian [a,*], Yanshan Yin [a], Yi Cheng [c,*]

[a] *School of Energy and Power Engineering, Changsha University of Science and Technology, Changsha 410114, China*
[b] *Department of Chemical Engineering and Applied Chemistry, Aston University, Birmingham B4 7ET, UK*
[c] *Energy and Bioproducts Research Institute (EBRI), Aston University, Birmingham B4 7ET, UK*

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ABSTRACT

The present work investigated the coupling pretreatment of acid washing and torrefaction to address secondary cracking of target products and condensation of intermediates and improved bio-oil quality and hydrocarbon selectivity of the catalytic fast pyrolysis (CFP) process. The total hydrocarbon yields in CFP increased from 28.06 wt% to 55.31 wt% by torrefaction and 46.29 wt% by coupling pretreatment. The acid washing resulted in fewer acids and phenols and more sugars in bio-oil by decreasing the AAEMs. The removal rate of the potassium was up to 96.7 %, and other elements were above 83 %. Torrefaction elevated the C/O ratio and the higher calorific value of biomass. It could also decrease the acid content in obtained bio-oil in the CFP process. In addition, the TG/TGA results showed that higher torrefaction temperature decreased the total weight loss of biomass. Meanwhile, the acid washing pretreatment improved the resolution of the two pyrolysis peaks of the DTG curve. These results showed that the AAEMs removal and intermediates inhibition could elevate the selectivity of the valuable chemical.

1. Introduction

China has promised the carbon emissions transition from peak to Net Zero within 30 years (Zhang and Chen, 2021). Renewable resources as alternatives are requested to petroleum for decreasing or recycling carbon. The abundant biomass waste is an ideal resource to achieve a low-carbon economy for energy harvesting, emissions reduction, and environmental safety (Campuzano et al., 2019; Hoang et al., 2021). Up to 155 million tonnes of wheat straw is generated as agricultural waste annually in China (Fang et al., 2022). The policies from the central government has led to the rapid development of the comprehensive utilisation of straw. However, it still has several problems, such as high cost of use, low utilisation rate and unreasonable industrial structure (Cheng et al., 2020; Li et al., 2018). Catalytic fast pyrolysis (CFP) is a promising way for agriculture waste valorisation by combining fast pyrolysis with the catalytic reforming process (Liang et al., 2021). The HZSM-5 zeolite appears to be an excellent catalyst for CFP because its porous structure and acid strength are beneficial to bio-oil and aromatics selectivity (Tian et al., 2022). However, the deactivation of the catalyst in the CFP process hinders the development of this technology (Liu et al., 2021). Residual carbon deposition was the principal cause of the catalyst deactivation. Different factors within the process, such as metal ion catalysis, molecules polycondensation, and others, may result in carbon deposition. (Che et al., 2019).

Light aromatics such as benzene, toluene, and xylene (BTX) were value-added platform chemicals for synthetic resins, plastics, fibres, rubber, and dye production. Conventional BTX was from the secondary processing of non-renewable fossil fuels (Che et al., 2019). Recently, the production of BTX from biomass by CFP process has received increasing attention. The formation of aromatics went through the Diels–Alder reaction. Furan derivatives and the olefin were the raw materials for BTX production (Wang et al., 2019a,b). Hence, increasing the sugar content is the key to promoting BTX conversion as sugar dehydration for furan derivates formation. In the CFP process, pretreatment technology could improve the characteristics of pyrolysis oil to produce more sugars by affecting the physicochemical properties of biomass (Wang et al.,

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* Corresponding authors.

E-mail addresses: tianh1103@163.com (H. Tian), y.cheng8@aston.ac.uk (Y. Cheng).

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2021). The workable pretreatment would reduce the cost based on the efficiency according to the characteristics of biomass feedstock.

Wheat straw has various AAEMs, like K, Na, Ca, and Mg, which are the essential elements for growth. In the CFP process, these AAEMs might cause uncontrolled reactions by replacing zeolites acid sites. Acid washing could promote the CFP process by removing most AAEMs (Wang et al., 2019a,b). This process can decrease the catalytic effect of AAEMs on the C-C bonds, promote L-glucan and aromatics production, and reduce the generation of coke and oxygenates (Verma et al., 2021). The selection of acid washing solutions mainly includes inorganic and organic acids, such as sulphuric acid, hydrochloric acid, nitric acid, and acetic acid. In addition, acid washing reduces the acidity of bio-oil by degrading most of the hemicellulose in biomass to inhibit the formation of acetic acid (Ji and Jin, 2016). Chen et al. (2019a) treated sweet sorghum bagasse with hydrochloric acid and found that acid treatment increased the yield of volatiles and bio-oil by removing most of the metals. Even though acid washing is favourable for the formation of pyrolysis oil, it will reduce the economy of pretreatment technology. In addition, excessive acid washing might change the structure and composition of the cell wall and introduce some unnecessary elements, such as Cl and S (Cen et al., 2019; Zhang et al., 2016).

Another restriction of the wheat straw CFP process was the instability of intermediates from hemicellulose and lignin degradation. In the cell walls of wheat straw, arabinoxylans are the main polysaccharide of hemicellulose. Ferulate bridge hemicellulose and lignin together form the lignin-carbohydrate complex (LCC) (Huang et al., 2020). This structure is easy to decompose at pyrolysis temperature for active acid, aldehyde or ketone, and phenolic generation. Torrefaction is a mild method to reduce the active intermediates by using medium or low temperature (200 ~ 300 °C), atmospheric pressure, or inert gas (Chen et al., 2015c). The partial degradation of hemicelluloses and lignin suppressed the polycondensation by intermediate products (Zhao et al., 2018). Torrefaction gives biomass a higher energy density and calorific value, better grind ability, and lower water absorption in the open air (Chen et al., 2015b).

In cotton stalk torrefaction, the torrefied biomass has lower oxygen content, higher carbon content and heating value than the raw material (Chen et al., 2015a). However, the yield of bio-oil decreases while the biochar rapidly increases with increased torrefaction temperature. Torrefaction has little effect on the chemical composition of biochar. Louwes et al. (2017) used mixed waste wood for torrefaction at different temperatures. When torrefied at 265 °C, the yield of bio-oil was the highest, along with the mass fraction of oxygen decreased to 37.2 %, and the calorific value increased to 23.1 MJ/kg. However, it has shown the enrichment of AAEMs in biomass raw materials.

By coupling acid washing and torrefaction, it might reduce the inhibition of AAEMs and intermediates to herbaceous crops pyrolysis for improving the quality of products. In the research of rice husk, the coupling pretreatment of acid washing and torrefaction increased the content of carbon elements and the high heating value (Zeng et al., 2019). Chen et al. (2017a) upgraded the method by coupling aqueous phase bio-oil washing and torrefaction for pretreatment to optimise the quality of biomass raw materials and pyrolysis products. The results showed the elimination of two pyrolysis peaks in the differential thermogravimetric (DTG) curve after metal removal, along with an elevation of bio-oil yield and pyrolysis products quality.

Presently, few reports have concentrated on promoting the CFP process of herbaceous crops by coupling various pretreatment methods. As reviewed above, the coupling pretreatment has noticeable improvements for pyrolysis products, specifically on bio-oil quality, by eliminating the unfavourable compositions to pyrolysis in the raw material. Interestingly, pretreatment might also favour the CFP process of herbaceous crops. In this study, investigations of acid washing and torrefaction pretreatment methods were evaluated for the wheat straw CFP process with an HZSM-5 catalyst. Py-GC/MS and tubular furnace tracked the properties of the wheat straw before and after pretreatment. A comparison between stand-alone and coupled pretreatment processes on wheat straw were made by analysing the product quality, especially bio oil composition, for non catalytic fast pyrolysis and CFP.

2. Materials and methods

2.1. Materials and catalysts

The wheat straw was from Lianyungang city, Jiangsu province, China, of which the particle size was under 0.74 nm (200 mesh) after cutting, crushing, and sieving. The HZSM-5 molecular sieves for catalytic pyrolysis were from the China University of Petroleum. Its silicon to aluminium ratio was 30, with a surface area of 394.5 m^2/g. The pore capacity of the catalyst was 0.2793, and the pore size was 2.832 nm. The wheat straw was dried in an electric heating oven at 105 °C for 12 h. The catalysts, HZSM-5, were calcined in a muffle furnace at 450 °C for 5 h before the experiments.

2.2. Pretreatment procedures

A nitric acid solution with a volume fraction of 7 % was used as the acid washing solution. In each experiment, 10 g of dried wheat straw was added to 200 mL of the nitric acid solution for acid washing. The resulting pulp was continuously stirred with a magnetic stirrer at 75 °C for 2 h, and then the supernatant was removed after standing for 10 min. Afterwards, the filter cake was washed with deionised water until the pH value of the washing solution was close to 7. The drying of the filtered cake was in an oven at 105 °C for 12 h. Samples indicated with the letter W in their sample name went through acid washing.

The torrefaction was conducted in the vertical tube furnace of which setting temperatures were 230 °C, 260 °C, and 290 °C. The carrier gas was high-purity nitrogen (99.999 %) with a flow rate of 200 mL/min. The tube furnace was heated to the set temperature, and the sample was placed in the tube furnace for 30 min. All samples that went through torrefaction have the letter T and the torrefaction temperature in their sample names. The quantitation of bio-oil and biochar were using electronic balance to measure their yields, and the gas was by differential subtraction. The units of these compounds were according to the dry-basis with ash-free.

2.3. Sample characterisation

The digestions of original and pretreated biomass were carried out using the wet digesting method. Each conduction loaded 0.5 g of the sample into 10 mL of concentrated nitric acid (AR) and 2 mL of hydrogen peroxide solutions and kept overnight for pre-elimination. Afterwards, the slurry was heated slowly on the control electric heating plate to prevent the solution from boiling. The iCE3000 series Atomic Absorption Spectrometer (ThermoFisher Ltd) was used to determine the concentrations of AAEMs in the digestion solutions. In addition, ultimate analysis (Elementar Varioel III) was used to trace the changes of elemental compositions of C, H and O in the wheat straw samples before and after pretreatment. The alkali metal removal rate was defined as follows:

$$\alpha_{\mathrm{p}} = \frac{\mathrm{m}_c - m_e}{m_c} \times 100\% \tag{1}$$

Where: α_{p} is the alkali metal removal rate, m_{e} and m_{c} denote the alkali metal content in the pretreated sample and the original sample, respectively.

Proximate analysis (SX-4–10 of Changsha Zhonghua electric furnace plant) was carried out according to the GB/T28731–2012 to obtain the composition of ash, volatiles and fixed carbon. Calorific values were calculated using Dulong formula:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash \quad (2)$$

The thermogravimetric analysis (TGA, STA 449F3 Jupiter) instrument characterised the effects of pretreatment on biomass pyrolysis. In each run, approximately 10 mg of samples were loaded and heated at a rate of 20 °C/min, from 30 °C to 900 °C. High purity nitrogen (99.999%) maintained an inert atmosphere of the system with a flow rate of 40 mL/min. After the experiment, the system kept the flowing nitrogen for 30 min to remove the volatile components in the gas chamber.

2.4. *Pyrolysis analysis experiments*

The diagram shows the experimental setup of the self-built tube furnace. The furnace employed a quartz tube as a heating vessel with an inner diameter of 60 mm and nitrogen as the pyrolysis atmosphere with a 200 mL/min flow rate. A quartz boat (50 *35 *35 mm) carried samples for pyrolysis and was pushed into the heating area when the furnace reached the set pyrolysis temperature. Afterward, a U-tube collected thus obtained bio-oil, the gas bag absorbed gas compounds, and the quartz boat kept the biochar. Fig. 1.

The Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS; GC/MS-QP 2010 Ultra, Shimadzu, Japan; Pyroprobe 5200 pyrolyzer, CDS, USA) technique was used to investigate the effects of the pretreatment on the catalytic fast pyrolysis of wheat straw. In each test, the pyrolysis was conducted in the quartz tube with samples in the middle. Quartz cotton was placed at both ends to prevent the sample powder from being blown out by the carrier gas. The parameters of the pyrolysis were 10 °C /ms of heating rate, 20 s of the residence time, 500 °C of the final pyrolysis temperature, and 2 mg of the injection amounts. In addition, the GC column was RTX-5 (30 m × 0.25 mm × 0.25 µm) with a ramp rate of 6 °C/min from 40° to 280 °C after being maintained for 4 min and finally held for 5 min. The sample injection temperature was 280 °C by using a split injection mode with a split ratio of 50:1. The total flow rate was 54.1 mL/min with the carrier gas of high purity helium (99.99 %). Electron ionisation (EI) ion source in MS was 70 EV of energy level at the temperature of 270 °C. Last, MS scan ranged from 35 to 500 *m/z*, of which the scan time interval was 0.3 s, and the scan speed was 1666. The reference for peak identification was the NIST mass spectrometry library. In the CFP experiments, the pretreated biomass samples were separated from the catalyst by quartz cotton, with other experimental conditions remaining.

Pyrolysis experiments with a self-built tube furnace were used to access the results of the three-phase products. The temperature in the reactor was 500 °C, and the experiments were carried out in the nitrogen atmosphere. In each test, 3 g samples were loaded into the feeder and transported to the reactor for pyrolysis for 15 min, the ratio of catalyst to sample mass was 1:1. The yields of biochar and bio-oil were determined at the end, and mass differences defined the non-condensable gases. The catalyst and sample were separated by quartz wool during the experiment without complete mixing, and the pyrolyzed biomass was separated from HZSM by taking out the quartz wool after the conduction. Each sample was experimented with three times to ensure repeatability and reduce the difference in analysis results due to the influence of the external environment, instrument conditions, and operation methods. The selectivity calculation of each component was from the percentage of thus obtained bio-oil according to the GC/MS detection.

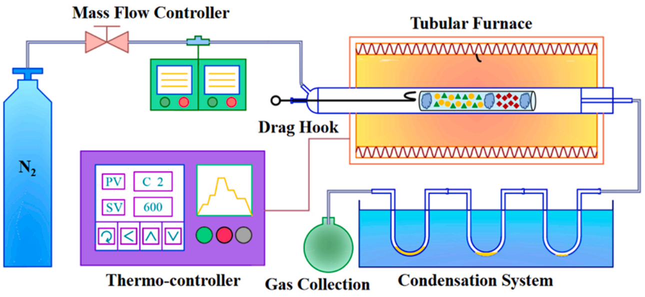


Fig. 1. The diagram of the catalytic fast pyrolysis experiment.

In summary, the samples with a pretreatment of torrefaction were named T-230/260/290, and the coupling pretreated samples were TW-230/260/290. The samples from the catalysis experiments were CT-230/260/290 and CTW-230/260/290, where the letter C indicates they were from the catalytic fast pyrolysis.

3. Results and discussion

3.1. *Effects of pretreatment on biomass properties*

3.1.1. *Proximate and ultimate analyses*

Table 1 shows the results of ultimate analysis, proximate analysis, and calorific value analysis of the wheat straw raw material and the samples after pretreatment. For the samples pretreated with torrefaction (T-230, T-260 and T-290), the proximate analysis results showed that the volatile matter content reduced with increased temperature, and the fixed carbon and ash contents showed an increasing trend. It was because torrefaction decomposed some hemicellulose in biomass and therefore reduced the volatile contents (Wang et al., 2016). Meanwhile, the more stable lignin increased the relative content of fixed carbon, which was the major product of lignin pyrolysis. Another relation of this change was the higher calorific value also increased. The volatile and fixed carbon content in acid-washed biomass increased and the ash content decreased. These observations refer to acid washing simultaneous removing ash and some organic matter from biomass, which inevitably leads to quality loss (Bhatnagar et al., 2022). Nitric acid is an inorganic acid that has been proved to be a significant agent in AAEMs removal from biomass (Dong et al., 2015). Moreover, in our previous study, we have explored the effects of different washing temperatures (25/50/75 °C), different pickling times (1–3 h) and different acid concentrations (3 %/5 %/7 %) of nitric acid on biomass pyrolysis. According to previous results, this work employed the most effective concentration of 7 % for the experiments. The ash contents of coupling pre-treated biomass (TWs) were less than torrefied biomass (Ts) and even lower than the original wheat straw. Among them, TW-230 reached the lowest ash content of 4.96 %. It confirmed that the coupling pretreatment of acid washing and torrefaction has the potential for ash content removal. It might offset the negative effect of the increase in ash content by torrefaction.

After acid washing and torrefaction the elemental composition of the samples changed, especially for the carbon and oxygen. The carbon content was increasing with higher torrefaction temperature. Meanwhile, the decrease in oxygen content and the mole ratio of O/C molecules. These changes showed that torrefaction had an acceptable deoxidation effect (Mei et al., 2016). In the T-290 sample, the carbon content increased to 47.28 % and the oxygen content and the mole ratio of O/C decreased to 48.27 % and 0.82 respectively. The composition was significantly different from the original wheat straw. The decrease in hydrogen content indicated potential hydrogen pathways from micromolecular to gaseous compounds, like H_2O, CH_4, C_2H_6, etc. Dehydration, decarboxylation, and decarbonylation would release many moistures, CO_2, CO, and more oxygenated carbohydrates (Klaas et al., 2020; Li et al., 2022). The removal of moisture and oxygen in the raw material also promoted the calorific value. Acid-washed samples also displayed similar tendencies. In acid-washed wheat straw and TW-290, the carbon content increased from 38.68 % to 47.82 %, and the oxygen content and the mole ratio of O/C molecules decreased to 47.22 % and 0.8 % respectively.

3.1.2. *Effects of pretreatments on AAEMs*

Table 2 shows the AAEMs content in biomass by different pretreatments. Acid washing could remove the AAEMs. The removal rate of

Table 1
The biomass properties of original and pretreated wheat straw.

Sample	Proximate analysis[a] (wt%)				Ultimate analysis[b] (wt%)				O/C	H/C	HHV[c] (MJ/kg)
	Moisture	Ash	Volatile	Fixed Carbon	C	H	O*	N			
Wheat straw	10.11	8.23	68.92	12.74	38.96	5.27	55.27	0.50	1.17	1.62	13.37
T-230	7.68	10.15	67.13	15.04	41.36	4.72	53.35	0.57	1.05	1.37	13.77
T-260	5.46	12.10	59.65	22.79	43.35	4.30	51.73	0.62	0.97	1.19	14.14
T-290	3.75	13.91	48.77	33.57	47.28	3.70	48.27	0.75	0.82	0.94	15.19
W	11.09	4.48	69.94	14.49	38.68	5.19	55.29	0.84	1.17	1.61	13.21
TW-230	7.26	4.96	72.21	15.57	40.35	4.78	54.02	0.85	1.09	1.42	13.52
TW-260	6.39	5.20	60.54	27.87	42.73	4.79	51.58	0.90	0.99	1.35	14.61
TW-290	5.03	5.77	56.73	32.47	47.82	3.72	47.22	1.24	0.80	0.93	15.67

[a] Air dried basis.
[b] Dry basis.
[c] Higher heating value on dry basis.
* Calculated by difference.

Table 2
AAEMs content before and after two-stage pretreatment (mg/kg).

Sample	K	Na	Ca	Mg
Wheat straw	2700.4	291.2	645.7	532
T-230	3162.5	304.9	678.8	853.7
T-260	3414.9	339.7	706.8	937.2
T-290	3847	371.9	770.4	1236.9
W	89.3	33.8	100.2	89.8
TW-230	80.1	61.6	122.8	80.5
TW-260	82.8	112.7	128.1	109.6
TW-290	134	142.3	174.3	128.4

potassium was up to 96.7 %, and the ones for sodium, calcium, and magnesium were all over 83 %. As the impurities have catalytic properties, AAEMs would re-polymerize degraded molecules and reduce pyrolysis oil yield (Hu et al., 2015). The results showed that acid washing had a promotional elution effect on AAEMs by dissolution, precipitation, and acid chemical removal. However, AAEMs contents in torrefied biomass increased since losing hemicellulose increased the ratio of AAEMs. As shown in Table 2, the contents of metal substances in TW samples keep the same tendency with the change of ash content in the sample. Hence, coupling pretreatment overcame the negative impact of torrefaction, reduced the metal content of wheat straw, and improved physicochemical properties of the biomass for further upgrading.

3.2. *Effects of pretreatment on CFP process and products*

3.2.1. *Effects of pretreatment on the yield of three-phase products from CFP process*

Fig. 2 illustrates the entire process of coupling pretreatment (a) and the effects on the yields of biomass CFP products (b). It shows that acid-washed biomass (Sample C-W) produced less biochar and more bio-oil than biomass without pretreatment (Sample C-R) in the CFP process. After the acid pretreatment, the bio-oil yield increased from 43.3 to

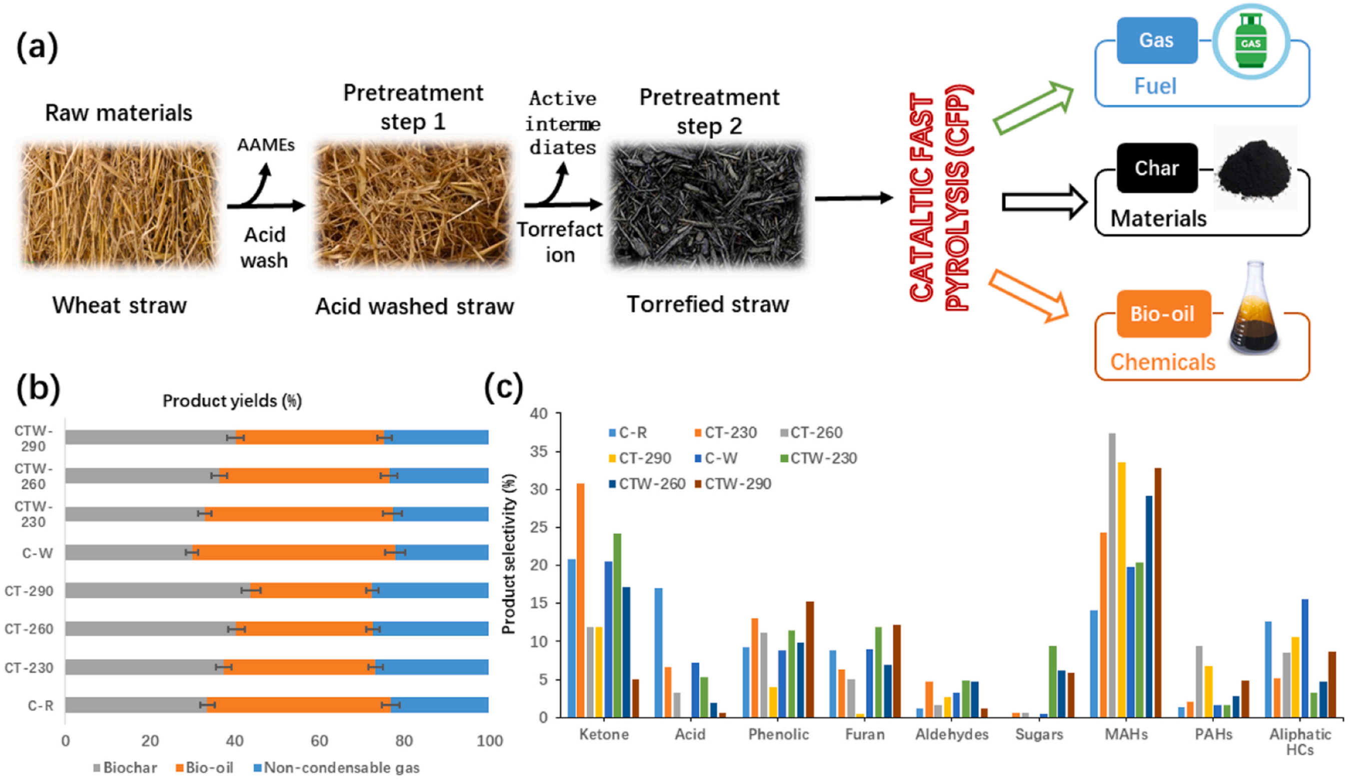


Fig. 2. The scheme of coupling pretreatment for wheat straw catalytic fast pyrolysis (a), and its products (b) and the liquid components (c) analysis under different pretreatment conditions.

48.0 wt%, and the biochar yield fell from 33.5 to 29.9 wt%. Meanwhile, acid-washing also led to a similar tendency for the samples with the same torrefied temperature. Those results implied that acid-washing was beneficial to liquid production. However, torrefaction pretreatment showed the opposite effects on liquid conversion. With the increased torrefied temperature, the bio-oil yields decreased from 43.3 to 28.6 wt% in unwashed samples (Sample CTs) and from 48 to 35.1 wt % in washed samples (Sample CTWs). This might be because the torrefaction removed parts of volatiles and therefore changed the ratio of final products. The CFP process comprises two steps. First, biomass thermally cracks into gases, including moisture, primary pyrolysis volatiles, and coke. The primary volatiles subsequently underwent a process of catalytic cracking to form light pyrolysis gases, such as H_2O, CO_2, CO, alkanes, olefins, and aromatics. Finally, it went through a series of reactions, like deoxidation, to yield the final liquids (Zhang et al., 2013). Torrefaction pretreatment removed parts of volatiles in advance and reduced the liquid generation in its following step.

3.2.2. *Effects of pretreatment on bio-oil composition*

Fig. 2c shows the products category results in the CFP process with more detail in Fig. 3, which presents the components analysis of wheat straw pyrolysis and CFP with and without pretreatment. A previous study showed that the HZSM-5 could effectively convert the unwanted oxygenated compounds in bio-oil into aromatics, such as benzene, toluene, and xylene (BTX) (Tang et al., 2019). The addition of HZSM-5 increased the monocyclic aromatic hydrocarbons (MAHs) contents up to 37.4 wt% (CT-260). It also grew the content of polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons after the addition of a catalyst. The PAHs are comprised of naphthalene, methylnaphthalene, ethyl naphthalene, dimethyl naphthalene, and indene. HZSM-5 promoted the production of such substances verifying its outstanding ability to deoxygenate bio-oil to form aromatic hydrocarbons. In addition, the pretreatment had a remarkable influence on the hydrocarbon contents. The content of aromatic hydrocarbons increased with the increase of torrefaction temperature both in washed and unwashed materials. However, the temperature turnover point emerged at 260 °C for acid-washed samples. The decrease of aromatic hydrocarbons implied the cross-linking or carbonisation at higher temperature torrefaction. Besides, the accumulation of AAEMs on the surface of ZSM-5 will inactivate the catalyst and reduce the aromatics generation (Mahadevan et al., 2016). The presence of AAEMs in biomass enhances the cracking and dehydration reaction in the pyrolysis process, increasing the thermally derived COx, coke, and reducing the aromatics and olefins (Wang et al., 2015).

In addition, the content of acids decreased significantly after coupling pretreatment both in the pyrolysis and CFP processes. As acids are corrosive, the coupling pretreatment was beneficial to produce bio-oil with better quality. Acids might be from the deacetylation of hemicellulose (Arteaga-Pérez et al., 2017). Torrefaction decomposed most hemicellulose and reduced the production of acids (Chen et al., 2018b). The decrease of acids might also promote gas production, such as CO_2 and CH_4.

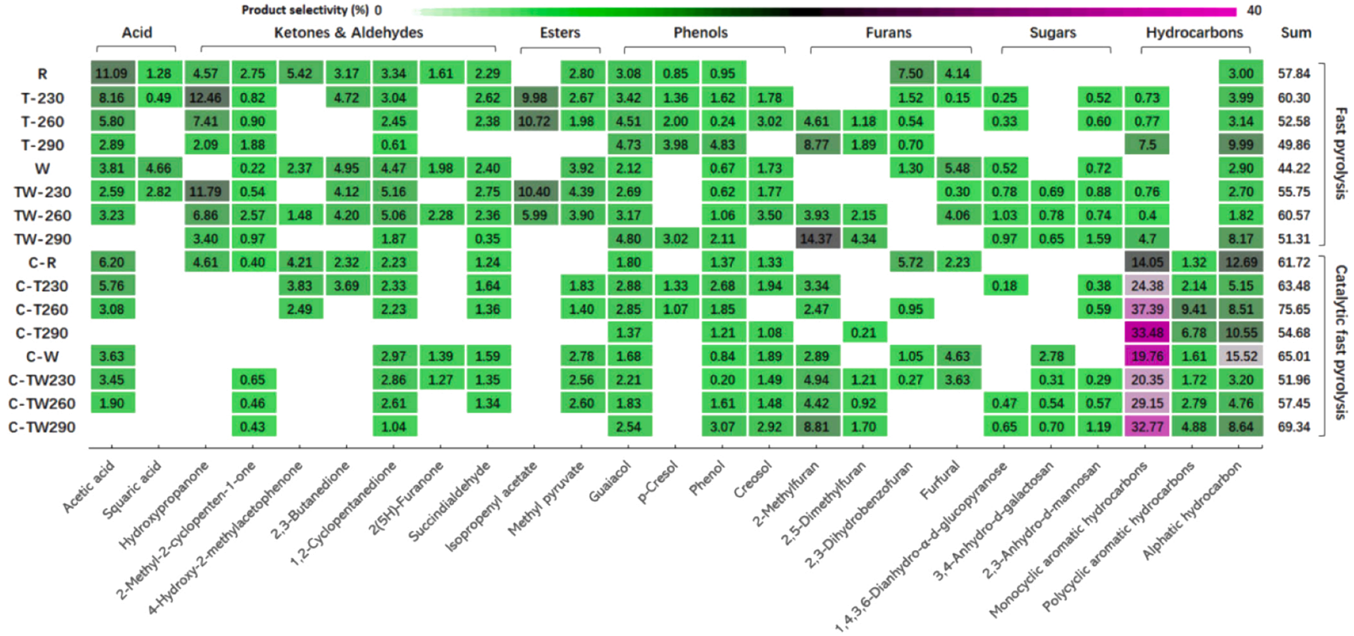
The pretreatment also promoted the production of sugars and furan derivates both in pyrolysis and CFP processes. Sugars and furan derivates came from the degradation of cellulose and hemicellulose macromolecules. The removal of the AAEMs might reduce the formation of coordination bonds with the oxygen atom of the hydroxyl group near the glucose ring. It makes the ring more stable and promotes low molecular weight oxygenates and sugar formation (Wang et al., 2015).

The amount of ketones and aldehydes had not changed with pretreatment conditions changing. As active intermediates, several factors would affect their change. The HZSM-5 could convert ketones and aldehydes into aromatic compounds through cyclisation and deoxygenation. The restriction of re-polymerisation has the possibility of releasing ketones and aldehydes. Hence, it requires further evidence to trace ketones and aldehydes. The same irregularity also appeared in the phenolic contents change under various pretreatment conditions. Phenolics should have a strong correlation with MAHs as they could generate aromatic hydrocarbons and olefins through the action of HZSM-5 active sites (Louwes et al., 2017). However, in this work, phenolic contents gave an irregular tendency which suggested the aromatisation of aliphatic components was the dominant way of MAHs formation in the CFP process.

3.3. *Unveiling the role of pretreatments*

3.3.1. *Effects of pretreatment on the yield of products from pyrolysis*

In most cases, the CFP process would undergo consecutive stages of



	Acid		Ketones & Aldehydes							Esters		Phenols				Furans				Sugars			Hydrocarbons			Sum	
	Acetic acid	Squaric acid	Hydroxypropanone	2-Methyl-2-cyclopenten-1-one	4-Hydroxy-2-methylacetophenone	2,3-Butanedione	1,2-Cyclopentanedione	2(5H)-Furanone	Succindialdehyde	Isopropenyl acetate	Methyl pyruvate	Guaiacol	p-Cresol	Phenol	Creosol	2-Methylfuran	2,5-Dimethylfuran	2,3-Dihydrobenzofuran	Furfural	1,4,3,6-Dianhydro-α-d-glucopyranose	3,4-Anhydro-d-galactosan	2,3-Anhydro-d-mannosan	Monocyclic aromatic hydrocarbons	Polycyclic aromatic hydrocarbons	Aliphatic hydrocarbon		
R	11.09	1.28	4.57	2.75	5.42	3.17	3.34	1.61	2.29		2.80	3.08	0.85	0.95				7.50	4.14						3.00	57.84	Fast pyrolysis
T-230	8.16	0.49	12.46	0.82		4.72	3.04		2.62	9.98	2.67	3.42	1.36	1.62	1.78			1.52	0.15	0.25		0.52	0.73		3.99	60.30	
T-260	5.80		7.41	0.90			2.45		2.38	10.72	1.98	4.51	2.00	0.24	3.02	4.61	1.18	0.54		0.33		0.60	0.77		3.14	52.58	
T-290	2.89		2.09	1.88			0.61					4.73	3.98	4.83		8.77	1.89	0.70					7.5		9.99	49.86	
W	3.81	4.66		0.22	2.37	4.95	4.47	1.98	2.40		3.92	2.12		0.67	1.73			1.30	5.48	0.52		0.72			2.90	44.22	
TW-230	2.59	2.82	11.79	0.54		4.12	5.16		2.75	10.40	4.39	2.69		0.62	1.77				0.30	0.78	0.69	0.88	0.76		2.70	55.75	
TW-260	3.23		6.86	2.57	1.48	4.20	5.06	2.28	2.36	5.99	3.90	3.17		1.06	3.50	3.93	2.15		4.06	1.03	0.78	0.74	0.4		1.82	60.57	
TW-290			3.40	0.97			1.87		0.35			4.80	3.02	2.11		14.37	4.34			0.97	0.65	1.59	4.7		8.17	51.31	
C-R	6.20		4.61	0.40	4.21	2.32	2.23		1.24			1.80		1.37	1.33			5.72	2.23				14.05	1.32	12.69	61.72	Catalytic fast pyrolysis
C-T230	5.76				3.83	3.69	2.33		1.64		1.83	2.88	1.33	2.68	1.94	3.34				0.18		0.38	24.38	2.14	5.15	63.48	
C-T260	3.08				2.49		2.23		1.36		1.40	2.85	1.07	1.85		2.47		0.95				0.59	37.39	9.41	8.51	75.65	
C-T290												1.37		1.21	1.08		0.21						33.48	6.78	10.55	54.68	
C-W	3.63						2.97	1.39	1.59		2.78	1.68		0.84	1.89	2.89		1.05	4.63		2.78		19.76	1.61	15.52	65.01	
C-TW230	3.45			0.65			2.86	1.27	1.35		2.56	2.21		0.20	1.49	4.94	1.21	0.27	3.63		0.31	0.29	20.35	1.72	3.20	51.96	
C-TW260	1.90			0.46			2.61		1.34		2.60	1.83		1.61	1.48	4.42	0.92			0.47	0.54	0.57	29.15	2.79	4.76	57.45	
C-TW290				0.43			1.04					2.54		3.07	2.92	8.81	1.70			0.65	0.70	1.19	32.77	4.88	8.64	69.34	

Fig. 3. Products selectivity for liquid component products. The sample name indicates Raw material (R), Torrefaction (T), Acid washing (W), and catalytic process (C). The numbers refer to torrefaction temperatures.

thermal degradation and gaseous conversion with heterogeneous catalysts. Hence, the investigation of non-catalytic pyrolysis would provide a deeper understanding of the role of pretreatment in this work. Fig. 4(a) shows the effects of pretreatment on the yield of biomass pyrolysis products. The observations of pretreatment condition change were similar to the ones for the CFP process. The acid-washed biomass has a higher bio-oil yield and lower char yield than the untreated wheat straw. This confirmed that the loss of AAEMs benefited bio-oil production and restricted char formation (Hu et al., 2015). However, the higher torrefaction temperature inhibited bio-oil production. The bio-oil yield decreased significantly from 45.85 % of W to 30.3 % of TW-290, along with the char yield gradually increasing. Several reasons might contribute to this result: first, torrefaction enriched the metal substances in wheat straw; the decomposition of hemicellulose reduced the formation of bio-oil in the subsequent pyrolysis of wheat straw and the carbonisation and cross-linking of cellulose contributed to the pyrolysis to char (Chen et al., 2019c). The coupling pretreatment also affected the pyrolysis products. Although the bio-oil production of coupling pretreatment was lower than the original wheat straw, it was higher than only torrefied pretreatment. The bio-oil yield of TW-290 increased by 3.14 %, the char yield increased by 1.21 %, and the gas yield decreased by 4.35 % when compared to torrefaction pretreatment.

3.3.2. *Effects of pretreatment on bio-oil components*

Figs. 3 and 4(b) give detailed information and categorise results on bio-oil components, which was helpful for further understanding the effects of pretreatment. Lignocellulosic biomass pyrolysis involved the thermal degradation of cellulose, hemicellulose and lignin (Lin et al., 2019). The D-glucopyranose is the block of cellulose and forms macromolecules by C-O-C connections. The decomposition of cellulose requires medium activation energy for L-glucose, 5-hydroxymethyl furfural, furfural, methylglyoxal, hydroxy-acetaldehyde, and acetic acid production (Chen et al., 2019c). Hemicellulose is the glycan with C-O-C linkages and with poor thermal stability. In addition, parts of ether linkages of lignin are unstable in heating to form macromolecule free radicals (Trubetskaya et al., 2020). The mass spectrum analysis of bio-oil might deduce the pyrolytic mechanism by tracing the intermediates of bio-oil with different pretreatment conditions.

As seen in the Fig. 4, detected compounds of bio-oil were ketones, acids, phenols, furans, aldehydes, esters, sugars, and other organics. Bio-oil from torrefied samples contained only a small percentage of sugar. Glucan is a potential platform chemical that can ferment to bioethanol and catalytically convert to fuels, chemicals, and pharmaceutical products. As known, AAEMs might cause secondary reactions of dehydration of sugars, carbon frame cracking, and glucose decomposition (Hu et al., 2015). Since acid washing removed AAEMs, the inhibition of AAEMs on glucose increased sugar content (Verma et al., 2021). The coupling pretreatment could combine the advantages of acid washing and torrefaction. In the torrefaction process, cellulose and hemicellulose carbonisation reduced the acids (Zeng et al., 2019). Meanwhile, the acid washing replaced AAEMs with protons and formed a loose structure, which improved the sugar selectivity.

The bio-oil from original biomass pyrolysis contained acids and showed acidic properties. However, the coupling pretreated biomass pyrolysis products had a lower acid content and acidic substances than the original biomass. Whilst, the acid content decreased with an increase in torrefaction temperature. Hemicellulose and cellulose pyrolysis facilitated acid formation. The torrefaction reduced the proportion of hemicellulose and restricted acid conversion. In addition, ketones are the active compounds and readily deteriorate the bio-oil. The increase in torrefied temperature first increased torrefaction in the bio-oil and then decreased at 260 °C. It showed that mild torrefaction effectively enhanced the stability of pyrolysis oil. In addition, the contents of hydroxy-acetone in acid-washed biomass pyrolysis were lower than the original wheat straw conversion. This implied the removal of AAEMs hindered the progress of the secondary cleavage and decreased the ketone content by the restricted intermediate secondary reaction.

Phenolics are potentially valuable products of lignocellulose pyrolysis which have various applications in many fields such as, material, food and medicine. The phenolic contents of torrefied biomass pyrolysis increased from 14.08 % of WS to 29.55 % of T-290 °C. The ether bond fracture and demethoxylation of lignin produced phenolics during torrefaction, resulting in the structure change (Ukaew et al., 2018). Torrefaction promoted phenol production as it was the main liquid product from lignin pyrolysis. The phenolic content of coupling pretreated biomass pyrolysis were higher than the acid-washed biomass and lower than the torrefied biomass. It reported that AAEMs linked lignin with cellulose and hemicellulose through weak bonds (Zhou et al., 2021). Hence, the decomposition of weak bonds of AAEMs would restrict the phenol conversion and inhibit lignin depolymerisation. It further enhanced the carbonisation of lignin and led to the reduction of phenol content.

Another observation was that the content of 2, 3-dihydro-benzofuran in bio-oil decreased with the rising torrefaction temperature. Torrefaction reduced the proportion of hemicellulose and moderated condensation and promoted the formation of furans. The furfural

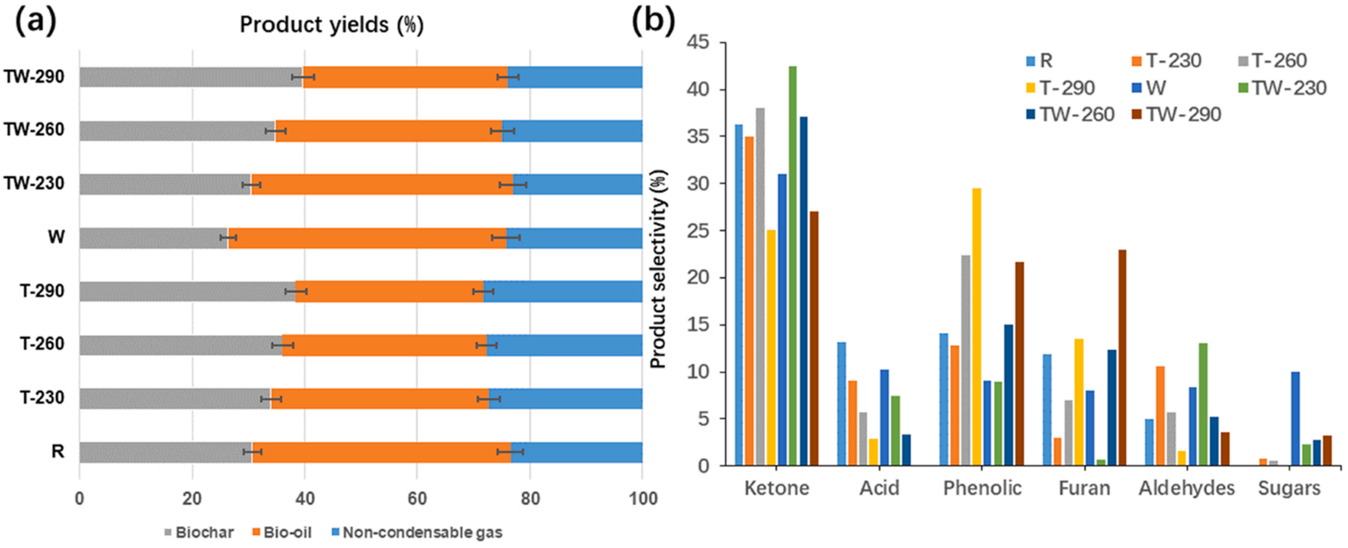


Fig. 4. The products (a) and the liquid components (b) analysis of wheat straw pyrolysis with different pretreatment conditions.

content of acid-washed biomass pyrolysis increased first and gradually decreased as the torrefaction temperature increased. Furfural is the product of polysaccharide depolymerisation and dehydration by pyrolysis (Chen et al., 2017b). A similar mechanism to sugar conversion, the acid-washing increased the loose composition of cellulose and hemicellulose which was beneficial to furans content increase. The high moisture and acid content were the dominant cause of high oxygen content, poor thermal stability and corrosivity for bio-oil. Deoxygenation in the pretreatment process reduced the moisture and acid content in the bio-oil and improved the aromatic compounds. It also reduced the subsequent upgrading cost by increasing the stability and calorific value of the biomass tar. In summary, the coupling pretreated biomass pyrolysis gave the lowest moisture and acid content and the highest HHV and phenolics content. These improvements correspondingly explained the mechanism of advantages in the subsequent catalytic pyrolysis processes.

3.4. *Effects of pretreatment on pyrolysis behaviours*

Fig. 5 shows the TG/DTG curves for the CFP processes of the samples before and after pretreatments. TG analysis showed that pyrolysis experienced 3 stages. First, the micro-weight loss process where water and small amounts of volatiles were evaporated. Next, DTG curves rapidly fell at about 250 °C. The decomposition of cellulose, hemicellulose and lignin was the crucial reaction at this stage. The final stage was from approximately 450 °C, along with the biomass carbonisation. In this period, residue decomposition was slow, and the pyrolysis was near completion, which showed flat curves on TG and DTG results (Chen et al., 2019b).

The TG/DTG curve of wheat straw has significant differences from torrefied biomass in weight loss. Since the dehydration was done in advance during torrefaction, the weight loss points for moisture evaporation decreased with torrefaction temperature. Therefore, the corresponding order for volatile analysis output was samples T-230, T-260, and T-290. The TGA curve of T-290 shows a very small amount of volatiles left in the sample after torrefaction at 290 °C. Similar tendencies of the DTG weight loss curves also expressed the decomposition of unstable compounds to various degrees. In addition, the TG/DTG curves also mirrored the ultimate analysis of biomass after pretreatment. The biomass without torrefaction performed conspicuous dehydration peaks, but the others showed slight weight loss before 200 °C. The volatile and fixed carbon showed the opposite tendency with the growth of the torrefaction treatment temperature, which was also related to the weight loss curves. More volatile with less fixed-carbon reserved fewer residues. Acid washed samples, of which volatiles up to 69.94 %, had the lowest residue rate of about 30 % on the TG curve. This value was about 65 % for TW-290 of 56.73 % volatile.

Observations from Fig. 5 was that coupling pretreatment of acid washing and torrefaction played a promotional role in the wheat straw pyrolysis. Previous studies have shown that metal species expressed strong catalytic effects on biomass pyrolysis, resulting in less bio-oil and more biochar (Lin et al., 2019; Zhang and Xiong, 2016). Presently, the maximum loss rate change moved the turnover points to the right with the increased torrefied temperatures. Acid washing removed most of the metal substances in biomass, thus reducing the catalytic effect of these metals and improving the thermal stability. Torrefaction then decomposed unstable compounds which also resulted in thermal stability improvement. Residual cellulose and hemicellulose promoted the formation of liquid pyrolysis products (bio-oil), while lignin contributed to the formation of solid pyrolysis products (biochar) (Chen et al., 2018a). Therefore, the final residue of the sample increased after torrefaction pretreatment.

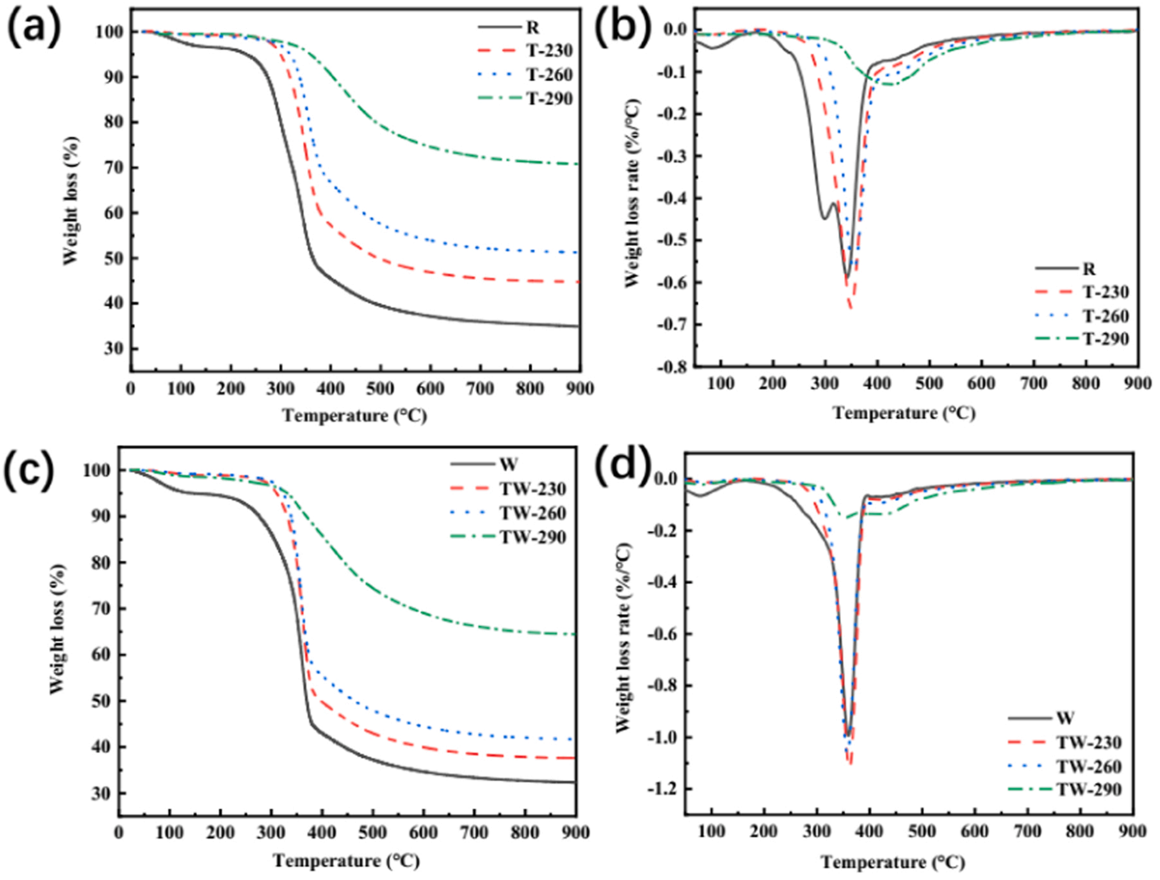


Fig. 5. TG (a and c) and TGA (b and d) results of different samples with different pretreatment conditions.

The DTG curve of raw material expressed an extra side peak. It implied the hemicellulose and cellulose difference between raw and pretreated biomass (Chen et al., 2019b). Hemicellulose was a heterogeneous polymer with a random and amorphous structure. Cellulose was a macromolecular polysaccharide composed of glucose with a stable frame. Therefore, hemicellulose was more active and unstable than cellulose. The low-temperature stage degraded hemicellulose, followed by the high-temperature stage degrading cellulose (Zhao et al., 2018). However, both torrefaction and coupling pretreatment tests eliminated the first shoulder of curves which implied that torrefaction reduced the side peak by hemicellulose removal.

4. Conclusions

The coupling pretreatment facilitated the physicochemical properties and the CFP process selectivity of wheat straw for valuable chemicals and fuel productions. The liquid components and thermal behaviours analysis expressed the advantages of acid washing and torrefaction and concluded that:

1. Acid washing removed most of the AAEMs in the original sample and improved the combustion characteristics of raw materials. The removal rates of potassium, sodium, calcium, and magnesium in biomass were 96.7 %, 88.4 %, 84.5 %, and 83.1 %, respectively. Meanwhile, the ash content decreased by 39.7%. In addition, acid washing facilitated liquid production and restricted solid conversion;
2. Torrefaction elevated the C/O ratio and the high calorific value of biomass. The trend of increasing hydrocarbons content slowed down with the torrefaction temperature increase. This process would decompose some hemicellulose to prevent re-polymerization from degraded intermediates. However, excessive pretreatment promoted solid production and decreased the liquid and gas conversion;
3. The coupling pretreatment addressed the condensation caused by AAEMs and intermediates and improved bio-oil quality and hydrocarbons selective of the CFP process. It reduced O/C, and O/C continued to decrease with the torrefaction temperature elevation. The TW-290 reduced O/C by 31.62 % compared with the original wheat straw. The components analysis showed that the coupling pretreatment benefited sugars conversion, meanwhile decreased phenols, acids, and ketones production. Hence, it showed the impetus of AAEMs and partial hemicellulose removal on lignocellulose catalytic pyrolysis.

CRediT authorship contribution statement

Xiong Gao: Conceptualization, Methodology, Validation, Investigation, Writing - original draft; **Zhen Zhou**: Validation, Investigation, Writing - original draft; **Brad Coward**: Writing -review & editing; **Jiawei Wang**: Project administration, Writing - review & editing; **Hong Tian**: Writing - review & editing, Project administration, Resources; **Yanshan Yin**: Funding acquisition, Resources; **Yi Cheng**: Funding acquisition, Conceptualization, Writing - original draft, 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.

Data availability

No data was used for the research described in the article.

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