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Washing pretreatment with light bio-oil and its effect on pyrolysis products of

bio-oil and biochar

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Abstract:

Rice husk is an abundant agricultural waste and the common disposal method of rice husk could cause serious environmental and human health problems. In this study, it was attempted to be converted into value added bio-based products such as bio-oil and biochar by washing pretreatment with light bio-oil followed by fast pyrolysis. It can be found that washing pretreatment with light bio-oil effectively removed a large amount of alkali and alkaline earth metals (AAEMs), and it has higher removal efficiency than HCl aqueous at the same pH of 2.8 because phenolic compounds in light bio-oil promoted the removal of some AAEMs. Furthermore, pyrolysis of washed rice husk with light bio-oil resulted in the increase of bio-oil yield and the decrease of water and biochar yields. GC/MS analysis indicated that light bio-oil washing pretreatment prior to fast pyrolysis process has an important effect on the quality of bio-oil, which resulted in significant increase of relative content of levoglucosan in bio-oil along with a reduction of low molecular weight compounds. Biochar, produced in higher yield, has

high silica content and high surface area, they have the potential to produce amorphous silica as well as adsorbent or catalyst support. This work revealed a promising process system to convert biomass waste into quality bio-based products.

Keywords: rice husk; washing pretreatment; fast pyrolysis; bio-oil; biochar

1. Introduction

Biomass has received considerable attention because of its renewability, carbon neutrality and low emissions of pollutants. Therefore, biomass is playing a significant role as an alternative source for energy and fuel production around the world. According to recent estimations the global production of rice is around 685 Mt, with production of rice husk per kg harvested being between 0.2 and 0.33 [1]. Rice husk is usually handled as a waste and burnt in open fields, but this practice involves serious environmental and human health problems due to the formation of fine crystalline silica particles. Therefore, the use of rice husk for energy not only reduces pollution, but also generates economic benefits.

Fast pyrolysis is considered as one of the most promising technologies for the thermo-chemical conversion of rice husk to bio-based products, such as biochar, bio-oil and syngas. It has been reported that several factors may influence the pyrolysis behavior of rice husk, such as the conversion units, the operating conditions and the chemical composition of the species [2,3]. Several studies have pointed out the properties of pyrolysis products significantly dependent on the amounts of its primary components (cellulose, hemicellulose and lignin) and inorganic species [4,5]. Meanwhile, it has been

reported that the existence of some interactions between the main biomass components that affect the pyrolysis behavior [6]. A challenge remains because of a large amount of inorganic species remaining in biomass, especially for agriculture residues, which usually contains high contents of alkali and alkaline earth metals (AAEMs) [7]. On one hand, it is well-known that AAEMs in biomass have significant impacts on pyrolytic pathways, decreasing the bio-oil yield and increasing the biochar yield. Furthermore, AAEMs can promote the formation of more water and organic acids, lowering bio-oil quality [8,9]. On the other hand, K and Na, along with S and Cl, are known to cause environmental and technological problems during combustion and gasification such as slagging, fouling and high temperature corrosion [10]. Thus, the removal of metallic species, in particular, that of AAEMs, prior to pyrolysis is an important pretreatment method of rice husk.

It has been known that water washing is a simple and effective pretreatment method to remove a large amount of of troublesome elements (K, Cl and S) from biomass [7,11]. But water-soluble metallic species account for no more than 30-80% of the total because of the presence of organically bound species in forms of carboxylates and inorganic minerals [12]. In addition, acidic medium, such as mineral or organic acids, has been reported had higher efficiency on removal of AAEMs [13]. However, use of the mineral acid is not reasonable in practice, because introducing undesirable P, Cl, S and N et al. into the pretreated biomass, contaminating the final products. Employment of organic acid (i.e. acetic acid) for washing biomass is not necessarily feasible from an

economical point of view. Bio-oil produced from pyrolysis of biomass that is often a homogeneous mixture of water and organic matter rich in acetic acids and non-acids [14]. In addition, high water contents in bio-oil can easily lead to phase separation into an aqueous and an organic phase. Thus, the light bio-oil (namely aqueous phase) have potentials as agents for leaching of AAEMs. According to Oudenhoven et al. [15], they recently proposed an application of utilization organic acids produced in the pyrolysis process itself to reduce the AAEMs content in woody biomass, resulting in the increase in bio-oil and levoglucosan yields after pyrolysis. In addition, the leaching of AAEMs from rice husk with bio-oil from the pyrolysis of the same rice husk has also been reported [16]. These previous studies achieved remarkable advances in understanding washing biomass with bio-oil obtained from its pyrolysis. However, the effects of washing with light bio-oil on the yield and quality of pyrolysis products of rice husk has not been fully investigated.

In this work, rice husk was used as raw material for investigating the effect of washing pretreatment with light bio-oil on the fuel properties and the removal efficiency of metallic species in biomass. And then fast pyrolysis experiments of washed rice husk were performed using a fixed-bed pyrolysis reactor. The yield and quality of bio-oil and biochar products were analyzed, in order to provide data for biomass pyrolysis and for further utilization of biomass resources.

2. Materials and methods

2.1. Materials

The biomass feedstock of rice husk was collected from Yangzhou city, Jiangsu Province, China. Prior to the experiments, rice husk samples used in this study were ground in a knife-mill and sieved to obtain a particle size fraction of 1-2 mm, then dried further at 105 ^{o}C for 12 h. The dried rice husk is denoted as RH.

2.2. Washing experiment

The light bio-oil used in this study was obtained from pyrolysis of rice husk at 550 ^{o}C in microwave pyrolysis reactor. Detailed descriptions of microwave pyrolysis system can be found elsewhere [17,18]. The aqueous phase (namely light bio-oil) was selected because it was of good flowability and has the pH of 2.8. The water content of the light bio-oil was determined by Karl Fischer titration and its chemical composition was analyzed by gas chromatography/mass spectrometry (GC/MS, Agilent 7890A/5975C). It was found that light bio-oil was a homogeneous mixture of water and organic matter. The moisture content of light bio-oil is 60.5%. It can be seen from **Table 1** that acetic acid was the most abundant and representative acid in light bio-oil, and some phenols can be detected by GC/MS in light bio-oil. For comparison also an aqueous solution of HCl (pH 2.8) was used for washing RH in this study.

Washing experiment was performed by leaching 15g RH in 150 mL light bio-oil at 30 ^{o}C with stirring for 4 h. After washing, the sample was filtered and then rinsed with deionized water until the pH of the effluent solution was neutral. After that wet sample was dried at 105 ^{o}C for 12 h to constant weight. In addition, the contents of inorganic species contained in samples before and after washing were determined using ICP-OES

(Leeman Labs Inc., USA) [17]. The tests were repeated three times under the same conditions for confirming the reproducibility. The removal efficiency (X_i) of metallic species by washing is defined as:

$$X_i = (1 - \frac{m_w R_{i,w}}{m_o R_{i,o}}) \times 100\% \tag{1}$$

Where i stands for the removed metallic species, m_w is the mass of the washed rice husk sample (g), m_o is the mass of the original rice husk sample (g), and $R_{i,w}$ and $R_{i,o}$ are the mass fraction of the metallic species in washed original rice husk sample (%), respectively. In addition, light bio-oil and aqueous solution of HCl washed rice husk samples are denoted as Bio-oil-RH and HCl-RH, respectively.

2.3. Fast pyrolysis experiment

Fast pyrolysis experiments were undertaken in a fixed-bed reactor system as shown in **Fig. 1**, which consists of ten components: nitrogen cylinder, mass flow controller, thermocouple, sample feeder, quartz reactor, electric furnace, temperature controller, condensing unit, moisture trap and gas sampling bag. The quartz fixed-bed reactor (450 mm length, 38 mm inner diameter) was placed inside a 3 kW electrical furnace which was controlled by the temperature controller to maintain the preset temperature. In this study, a K-type thermocouple with the diameter of 3 mm was played at the center of biomass packed bed to detect the temperature so as to provide a reference for temperature controller. The condensing unit which consists of three condensate collectors and ice-water bath was used to collect the liquid product. The non-condensable gas was collected in 10 L Tedlar® gas sampling bags.

For each experiment, in order to maintain an inert atmosphere, nitrogen with 200 mL/min flow rate was passed through the reactor for 15 min prior to the commencement of the experiment. When the temperature was reached and stabilized to the pyrolysis temperature (550 ^{o}C), original and washed rice husk samples (5 g) placed in the sample feeder in advance were fed into the quartz fixed-bed reactor. Thereafter, the rice husk samples were heated to the pyrolysis temperature rapidly, followed by holding for 10 min. Biochar and bio-oil yields were calculated from the direct weight of each fraction after the reaction completed, while gas yield was calculated by difference based on the mass balance. All experiments were carried out in three runs to confirm the values obtained, the average value was reported.

2.4. Analysis methods

The proximate analysis (ash, volatile matter and fixed carbon) of samples was carried out based on GB/T 28731-2012 standard of China. The ultimate analysis was determined with a Vario EL-III elementar (ELEMENTAR Analysensysteme GmbH). The higher heating value (HHV) was analyzed by the SDACM3000 calorimeter. In addition, absolute content of inorganic species contained in original and washed rice husk samples was determined using ICP-OES (Leeman Labs Inc., USA). Each analysis was repeated three times to ensure the accuracy of the results.

The chemical composition analysis of liquid products was carried out using gas chromatography/mass spectrometry (GC/MS, Agilent 7890A/5975C) with a Varian Cp-sil 8cb capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The carrier

gas (helium, 99.999%) was set at a constant flow rate of 3 mL/min. The temperature of oven was programmed from 40 to 180 ^{o}C at the heating rate of 5 ^{o}C/min, and then to 280 ^{o}C at the heating rate of 20 ^{o}C/min. MS was conducted in the following operational conditions: transfer line 230 ^{o}C, ion source 230 ^{o}C and electron energy 70 eV.

The physicochemical properties of biochar, such as proximate analysis, ultimate analysis and higher heating values, were also measured, and the potential utilization value of biochar was analyzed. In this study, the pore structure properties of the biochar were measured via nitrogen adsorption isotherm at 77 K with a Micromeritics instrument ASAP 2020. The specific surface area was analyzed using the Brunauer-Emmett-Teller (BET) model. In addition, chemical compositions of ashes obtained from biochar were carried out using XRF analysis (ARL-9800).

3. Results and discussion

3.1. Washing pretreatment with light bio-oil

3.1.1. Effect of washing on fuel properties

The fuel properties (proximate analysis, ultimate analysis and HHV) obtained from original and washed rice husk samples are presented in **Table 2**. As shown in **Table 2**, compared to RH, the ash content of HCl-RH and Bio-oil-RH decreased from 16.53% to 15.27% and 15.17%, respectively. Meanwhile, by washing pretreatment with HCl aqueous and light bio-oil the higher heating values of rice husk samples were increased slightly. In addition, reduction of the ash content made a main contribution to the increment of the heating value.

Previous studies have indicated that besides the inorganic components, some organic components could be leached out during the process of acid washing, which does happen when strong acids or higher temperatures (hydrolysis conditions) are applied [15]. However, in this study washing pretreatment performed at 30 °C for 4 h indicated that no significant amount of organic components were lost during washing. The results obtained from the FTIR spectroscopy of original and washed rice husk samples as shown in **Fig. 2** also confirmed it. A broad band located around 3440 cm^{-1} in the spectra was attributed to the stretching vibration of the O-H bonds [19]. The narrow band at 2800-3000 cm^{-1}, which was assigned to C-H stretching vibration, present in alkyl groups such as methyl and methylene groups [19]. The band around 1730 cm^{-1} corresponding to the C=O stretching vibration was mainly caused by free carbonyl groups, which was a typical hemicellulose marker [20]. The band located at 1610 cm^{-1} indicated the presence of C=C bonds of aromatic compounds. The peaks around 1200-1500 cm^{-1} were assigned to the C-H and C-H$_2$ stretching vibrations. The broad band observed around 1096 cm^{-1} may be attributed to C-O and Si-O-Si stretching, which were reasonably distinctive for RH, HCl-RH and Bio-oil-RH [21]. Two significant bands at 809 and 460 cm^{-1} indicated the presence of Si-O bonds in original and washed rice husk samples [21]. It can be observed that original and washed rice husk samples resulted in identical spectra confirming that there was indeed no significant loss of organic components during washing. That was because the organic contents had not been decomposed at the mild washing condition.

3.1.2. Effect of washing on leaching of metallic species

Fig. 3 shows changes in the removal efficiency of metallic species with washing time. It can be found that the removal efficiency of most metallic species remained unchanged when the washing time was longer than 4 h. Therefore, washing time of 4 h was selected in this study. **Fig. 4(a)** and **Fig. 4(b)** compared the relative content of metallic species and removal efficiency by washing pretreatment of rice husk samples, respectively. The K content of RH is outstanding higher than other metal contents, because of excess agricultural fertilization with common potash fertilizer in the local, and it can be also found in other agricultural wastes [7]. For washing pretreatment with light bio-oil, the removal efficiency of K, Na and Mg were up to 98.5%, 93.9% and 95.1%, nevertheless, the Ca, Fe and Al removal efficiency was 66.7%, 73.5% and 72.5%, respectively. It has been reported in previous report that the majority of K, Na and Mg were presented in the form of chlorides of metallic species and organically bound species that are ion-exchanged to acidic oxygen functionalities, which can be removed by acid washing easily [16]. However, a large amount of Ca, Fe and Al species were presented in the form of carbonates and silicates. In addition, it can be found that light bio-oil washing gave higher removal efficiency of almost all the metallic species except for Fe than HCl aqueous at the same pH. This can be explained that the abundance of acetic acid in light bio-oil is effective on removal of metallic species in rice husk samples. Furthermore, it is suggested that other components such as phenolic compounds in light bio-oil promoted the access of acetic acid to metallic species during

the process of washing pretreatment [16].

Therefore, compared to mineral acid, light bio-oil not only has the higher removal efficiency of metallic species in biomass, but also avoids introducing undesirable P, Cl, S and N et al. into the treated biomass, contaminating the final products. Employment of organic acid (i.e. acetic acid) for washing biomass is not necessarily feasible from an economical point of view. Furthermore, the used light bio-oil can be used to produce syngas by co-gasification with some carbonaceous material such as petroleum coke or coal [22,23]. The AAEMs contained in light bio-oil will play catalytic roles in the process of gasification [24].

3.2. Pyrolysis performance of original and washed rice husk samples

3.2.1. Product yields of original and washed rice husk samples

According to previous reports, it has been known that temperature is a key factor influencing the yields and compositions of pyrolysis products [25]. In this study, 550 $^{\circ}$C was selected as the pyrolysis temperature for maximum bio-oil yield in the fast pyrolysis process. The yields of biochar, bio-oil and gas products obtained from fast pyrolysis step of original and washed rice husk samples are presented in **Fig. 5**. The yields of biochar, bio-oil and gas products obtained from fast pyrolysis of original rice husk were 38.86%, 45.24% and 15.90%, respectively. Compared to the product yields from fast pyrolysis of original rice husk, it can be seen that washing pretreatment with light bio-oil increased the bio-oil yield from 45.24% to 52.76%, while decreased the biochar yield from 38.86% to 36.70%. It was noteworthy that washing pretreatment

with light bio-oil resulted in the larger bio-oil yield obtained from fast pyrolysis than washing with HCl aqueous.

These results can be attributed to the catalytic effect of metallic species on the pyrolysis process. As mentioned above, washing pretreatment with light bio-oil removed a large amount of metallic species especially AAEMs. It was found that K, Na, Ca and Mg increased the gas yield, decrease both the yield and molecular weight of the bio-oil. In addition, these metals behaved differently with regards to their catalytic effects on pyrolysis by concentration: K > Na > Ca > Mg [26]. Washing with light bio-oil had a higher removal efficiency of K, Na, Ca and Mg than washing with HCl aqueous, resulting in it has the larger bio-oil yield than washed rice husk with HCl aqueous.

3.2.2. Bio-oil analysis

To further investigate the effect of washing pretreatment with light bio-oil on fast pyrolysis of rice husk samples, the properties of bio-oil were investigated. The moisture content of bio-oil was measured by Karl-Fischer titration. It can be seen that moisture content decreased from 45.6% obtained from RH to 39.3% obtained from HCl-RH, and further to 38.4% obtained from Bio-oil-RH. Thus it can be observed that the yield of organic fraction in bio-oil was increased by washing pretreatment because of less intense dehydration reactions [27].

The GC/MS technique was conducted to analyze the chemical components of bio-oil, and the identified compounds are listed in **Table 3**. It is known that the GC/MS technique could not give the quantitative analysis of the bio-oil products, however, the

chromatographic peak area% is linear with its content [13]. The bio-oil obtained was a

complex mixture which contained a wide variety of oxygenated organic compounds,

and the compositions of bio-oil can be divided into seven main groups according to

their functional groups, such as acids, ketones, aldehydes, furans, phenols, sugars, and

others. The relative contents of different groups of bio-oil from fast pyrolysis of original

and washed rice husk samples are presented in **Fig. 6**. In comparison to original rice

husk, light bio-oil washed rice husk decreased the contents of acids, ketones, furans and

phenols. Meanwhile, the contents of sugars which are mainly derived from cellulose

pyrolysis were significantly increased for light bio-oil washed rice husk samples,

especially levoglucosan. It can be seen that the removal of AAEMs with washing

pretreatment affected the depolymerisation of cellulose, hemicellulose and lignin.

It can be seen from **Table 3** that the relative content of levoglucosan was about

3.5% from pyrolysis of original rice husk. This value obtained from fast pyrolysis of

light bio-oil washed rice husk was almost 9 times (28.4%) of that from fast pyrolysis of

original rice husk. Levoglucosan is an important and highly valuable chemical, which

can be used for polymer chemistry, pharmaceuticals, fermentation, and food

applications [15]. It has been reported that presence of relatively low concentrations of

AAEMs already reduced the levoglucosan yield to a large extent. It can be explained by

two aspects. Firstly, alkali metals (i.e. K and Na) actually promoted catalytic reactions

such as ring fission and fragmentation of a glucose unit, resulting in a lower yield of

sugars and a higher yield of low molecular weight compounds during fast pyrolysis.

Secondly, alkaline earth metals (i.e. Mg and Ca) bound in the form of carboxylates had

the effect of joining two parts of biomass structures together acting as crosslinks [9].

Furthermore, the ion-exchanging process during the process of washing with light

bio-oil resulted in the disintegration of these crosslinks in the biomass structure, which

would increase the yield of sugars and decrease the chance of reactions to form water [28].

Fig. 7 shows the distribution of compounds with different carbon atom amounts

(e.g., C4 represents all the compounds whose molecules contain four carbon atoms).

C2-C5 compounds mainly regarded as low molecular weight compounds such as acids

and ketones. C6 compounds mainly consisted of levoglucosan and levoglucosenone.

C7-C10 compounds, regarded as completely chain breaking decomposed products of

lignin in biomass. The C11+ compounds, the incompletely chain-breaking decomposed

products of lignin, accounted for only a small proportion in the bio-oils. The results

obtained from Fig. 7 revealed that the presence of AAEMs in rice husk samples

effectively promoted the chain-breaking decomposition of lignin to produce more

lighter compounds derived from lignin and decreases in the heavier lignin derivatives.

The removal of these AAEMs by washing pretreatment with light bio-oil would

decrease the crosslinking density of lignin structures to facilitate the release of large

lignin fragments as lignin-originated larger oligomers in the bio-oil [29]. It has been

reported that the AAEMs would act as crosslinks to stabilise the 3-D structure of lignin

or links between lignin and cellulose/hemicelluloses, causing further breakdown of

weak bonds to produce lighter components in bio-oil [9].

3.3.2. Biochar analysis

Biochar is the solid product obtained from fast pyrolysis of rice husk samples, which recently has gained attention for its economic value [18,30]. The biochar obtained from fast pyrolysis of original and washed rice husk samples is denoted as "RHC", "HCl-RHC" and "Bio-oil-RHC", respectively. **Table 4** shows the effect of washing pretreatment with light bio-oil on the physicochemical properties of biochar. The proximate analysis showed that ash content in the biochar decreased by washing pretreatment of rice husk samples, which was also reflected by the results of ultimate analysis. However, the ash content in biochar obtained from light bio-oil washed rice husk was up to 41.27%, which was much higher than other biochar [31]. Moreover, the higher heating value (18.85 MJ/kg for the biochar obtained from light bio-oil washed rice husk) was low compared to other solid fuels. In view of these results, it can be indicated that combustion of biochar obtained from rice husk samples was an undesirable option. As shown **Table 5**, the results of chemical compositions of ashes from biochar indicated that silica content was increased from 91.98 wt.% to 99.33 wt.% by light bio-oil washing pretreatment of rice husk. Due to its high silica content in biochar, biochar obtained from pyrolysis of light bio-oil washed rice husk can be an economically viable resource to produce amorphous silica [32].

The porous texture parameter is one of the crucial properties for biochar. It can be observed from **Table 4** that washing pretreatment with light bio-oil had a certain positive effect on the pore structure of biochar. The BET surface area of light bio-oil

washed rice husk biochar was 198.3 m^2/g, and that of HCl washed rice husk biochar was 177.8 m^2/g, while that of original rice husk biochar was only 117.0 m^2/g. It can be seen that biochar obtained from fast pyrolysis of light bio-oil washed rice husk had the largest specific surface area. The results may be inducted that washing pretreatment with light bio-oil removed a large mount of impurities and metallic species in rice husk, which was beneficial to the development of porous structure in biochar [33]. This could improve the performance of biochar for use as adsorbent or catalyst support [34].

4. Conclusions

The results obtained in this study indicated that washing pretreatment with light bio-oil effectively removed a large amount of AAEMs, and it has higher removal efficiency than HCl aqueous at the same pH. Furthermore, it can be found that pyrolysis of washed rice husk with light bio-oil resulted in an increased bio-oil yield and a decreased biochar and water yields. Light bio-oil washing pretreatment prior to pyrolysis process has an important effect on the quality of bio-oil, which resulted in significant increase of relative content of levoglucosan in bio-oil along with a reduction of low molecular weight compounds. Washing pretreatment with light bio-oil increased the purity of silica in biochar and the specific surface area of biochar, therefore it has the potential to be raw materials of amorphous silica as well as adsorbent or catalyst support.

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Figure captions

Fig. 1. Schematic diagram of fixed-bed reactor, which consists of (1) nitrogen cylinder, (2) mass flow controller, (3) thermocouple, (4) sample feeder, (5) quartz reactor, (6) electric furnace, (7) temperature controller, (8) condensing unit, (9) moisture trap, (10) gas sampling bag.

Fig. 2. FT-IR spectra of original and washed rice husk samples.

Fig. 3. Changs in removal efficiency of metallic species with washing time.

Fig. 4. (a) The relative content of metallic species of original and washed rice husk samples; and (b) the removal efficiency of metallic species by washing pretreatment.

Fig. 5. The product yields obtained from fast pyrolysis of original and washed rice husk samples.

Fig. 6. Relative contents of different groups in bio-oil from fast pyrolysis of original and washed rice husk samples.

Fig. 7. Distribution of compounds with different carbon atom amounts in bio-oil from fast pyrolysis of original and washed rice husk samples.

Tables

Table 1 The key compounds in light bio-oil.

Compounds	molecular formula	Relative content (%)
Acids		
Acetic acid	$C_2H_4O_2$	30.061
Propionic acid	$C_3H_6O_2$	0.524
Total		30.585
Ketones		
2-Propanone, 1-hydroxy-	$C_3H_6O_2$	9.139
1-Hydroxy-2-butanone	$C_4H_8O_2$	1.647
2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	1.786
1,2-Cyclopentanedione	$C_5H_6O_2$	2.471
1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$	2.745
Total		17.788
Aldehydes		
Butanedial	$C_4H_6O_2$	0.163
Total		0.163
Furans		
Furfural	$C_5H_4O_2$	3.667
2-Furanmethanol	$C_5H_6O_2$	2.997
2(5H)-Furanone	$C_4H_4O_2$	1.561
2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	0.241
Benzofuran, 2,3-dihydro-	C_8H_8O	2.185
Total		10.651
Phenols		
Phenol	C_6H_6O	2.502
Phenol, 2-methyl-	C_7H_8O	0.637
Phenol, 4-methyl-	C_7H_8O	3.321
Phenol, 2-methoxy-	$C_7H_8O_2$	4.132
Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	1.66
1,2-Benzenediol	$C_6H_6O_2$	2.834
1,2-Benzenediol, 3-methyl-	$C_7H_8O_2$	1.614
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0.906
2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	0.812
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	1.273
Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	0.461
Total		20.152

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Table 2 The fuel properties of original and washed rice husk samples.

Samples	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)				HHV (MJ/kg)
	A_d	V_d	FC_d	C	H	O	N	
RH	16.53	70.60	12.87	38.23	5.467	39.446	0.327	16.58
HCl-RH	15.27	71.88	12.85	39.41	5.354	39.608	0.358	17.13
Bio-oil-RH	15.17	71.75	13.08	41.04	5.319	38.148	0.323	17.20

Table 3 GC/MS analysis of bio-oil obtained from fast pyrolysis of original and washed rice husk samples.

Molecular formula	Compounds assignment	Area%		
		RH	HCl-RH	Bio-oil-RH
$C_2H_4O_2$	Acetic acid	14.732	9.606	7.340
C_2H_8OSi	Silanol, dimethyl-	0.369	0.465	0.595
$C_3H_6O_2$	Acetol(2-Propanone,1-hydroxy-)	6.943	4.294	1.359
$C_6H_{14}O_2$	Ethane,1,1-diethoxy-	0.993	0.961	0.694
$C_4H_8O_2$	1-Hydroxy-2-butanone	0.807	0.408	ND
$C_4H_6O_2$	Butanedial	1.059	1.748	0.626
$C_5H_4O_2$	Furfural	3.567	3.4	5.088
$C_5H_6O_2$	2-Furanmethanol	2.005	1.214	0.377
$C_5H_8O_3$	2-Propanone, 1-(acetyloxy)-	1.271	0.868	0.422
$C_4H_4O_2$	2(5H)-Furanone	0.543	1.089	0.491
$C_5H_6O_2$	1,2-Cyclopentanedione	3.454	2.71	0.766
C_6H_6O	Phenol	1.685	0.825	0.835
$C_6H_6O_3$	Levoglucosenone	0.596	1.748	4.214
$C_8H_{16}O_3$	Furan, 2,5-diethoxytetrahydro-	1.726	1.756	0.723
$C_6H_8O_2$	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.797	1.548	1.135
C_7H_8O	Phenol, 2-methyl-	0.791	0.467	0.454
C_7H_8O	Phenol, 4-methyl-	2.215	1.812	3.103
$C_7H_8O_2$	Phenol, 2-methoxy-	5.293	2.978	2.646
$C_9H_{18}O_3$	2-Pentanone, 5,5-diethoxy-	0.7	1.033	0.858
$C_8H_{10}O$	Phenol, 4-ethyl-	1.758	1.166	1.25
$C_8H_{10}O_2$	Phenol, 2-methoxy-4-methyl-	3.57	4.239	6.011
$C_6H_6O_2$	1,2-Benzenediol	2.104	1.233	0.753
C_8H_8O	Benzofuran, 2,3-dihydro-	7.161	6.009	4.989
$C_7H_8O_2$	1,2-Benzenediol, 4-methyl-	0.886	0.806	0.899
$C_9H_{12}O_2$	Phenol, 4-ethyl-2-methoxy-	2.406	1.671	1.613
$C_9H_{10}O_2$	2-Methoxy-4-vinylphenol	5.646	4.425	3.586
$C_8H_{10}O_3$	Phenol, 2,6-dimethoxy-	1.35	0.788	0.763
$C_{10}H_{12}O_2$	Eugenol	0.558	0.508	0.346
$C_8H_8O_3$	Vanillin	0.887	0.704	0.628
$C_9H_{12}O_3$	Phenol, 4-methoxy-3-(methoxymethyl)-	0.605	0.665	0.789
$C_{10}H_{12}O_2$	Isoeugenol	2.945	2.388	2.202
$C_{10}H_{14}O_2$	Phenol, 2-methoxy-4-propyl-	0.128	0.312	0.516
$C_6H_{10}O_5$	Levoglucosan	3.543	14.391	28.428
$C_{11}H_{14}O_3$	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.6	1.068	1.464
$C_{16}H_{16}O_4$	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin	0.383	0.528	0.626

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Table 4 Physicochemical properties of biochar obtained from fast pyrolysis of original and washed rice husk samples.

Samples	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)				HHV (MJ/kg)	S_{BET} (m²/g)
	A_d	V_d	FC_d	C	H	O	N		
RHC	45.05	14.17	40.78	44.73	1.80	7.69	0.73	17.68	117.0
HCl-RHC	42.00	15.19	42.81	46.44	1.81	6.92	0.83	18.32	177.8
Bio-oil-RHC	41.27	14.30	44.43	47.89	1.85	6.13	0.76	18.85	198.3

Table 5 Chemical compositions of ashes obtained from biochar.

Constituent	RHC (wt.%)	HCl-RHC (wt.%)	Bio-oil-RHC (wt.%)
SiO_2	91.98	98.21	99.33
K_2O	3.44	0.57	0.030
CaO	0.90	0.56	0.30
SO_3	0.52	0.093	0.096
P_2O_5	0.45	0.098	0.12
MgO	0.32	0.16	0.004
Fe_2O_3	0.21	0.064	0.041
MnO	0.21	0.16	0.028
Al_2O_3	0.076	0.043	0.030
Cl	0.046	0.008	0
Cr_2O_3	0.020	0.009	0.006
Na_2O	0.067	0.005	0.005
ZnO	0.009	0.010	0.004
CuO	0.003	0	0.002
TiO_2	0.002	0	0
NiO	0.001	0.005	0.001
Others	1.75	0.010	0.001

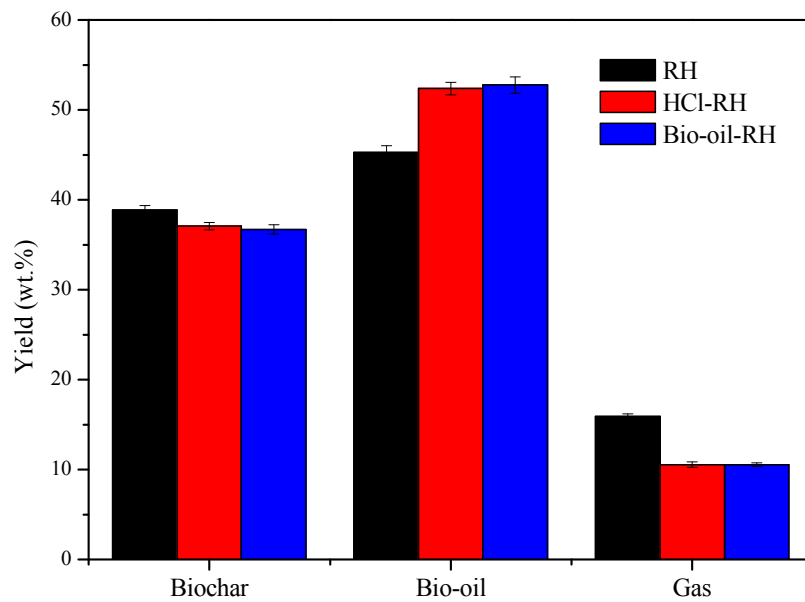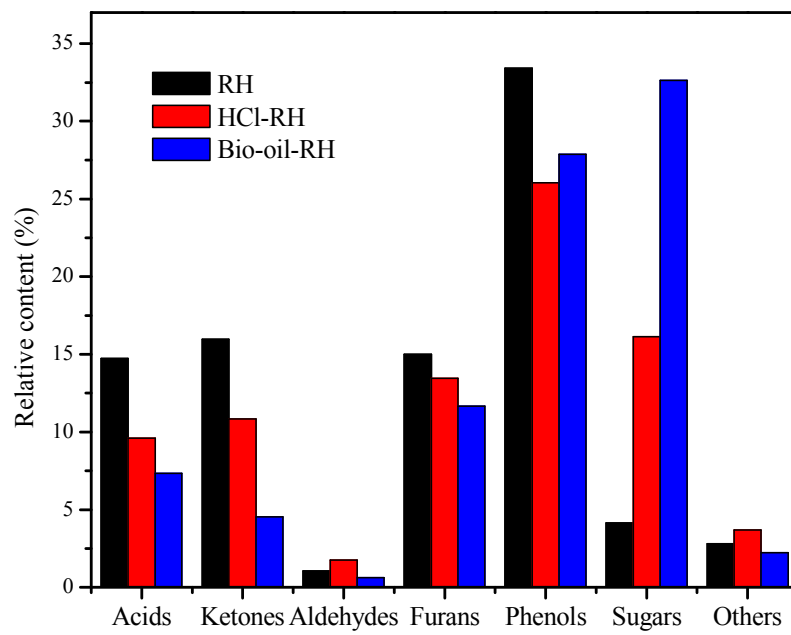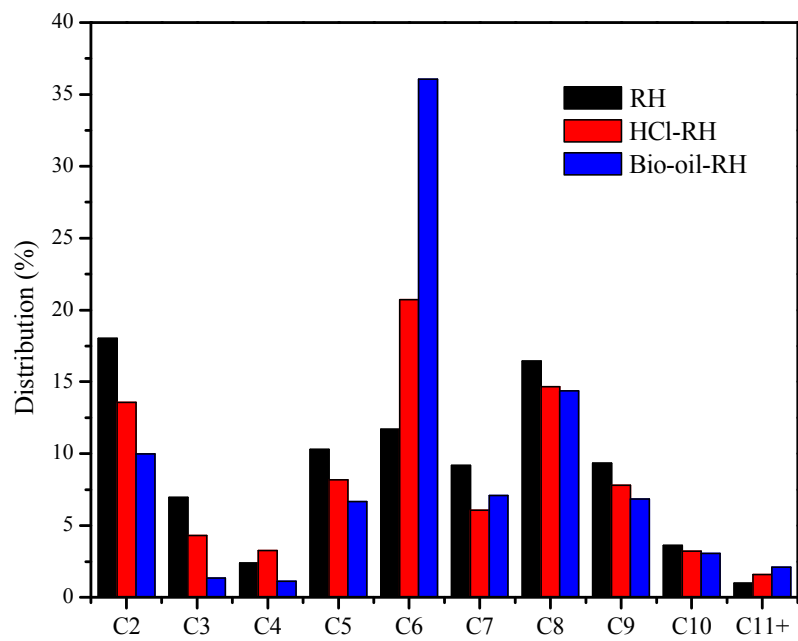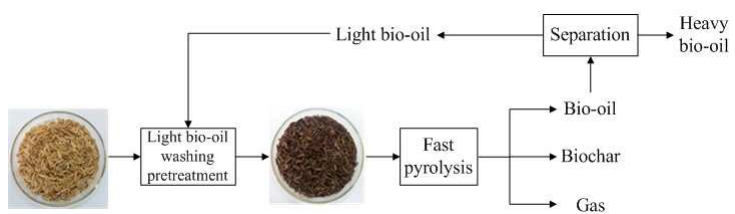**Figures**
Fig. 1
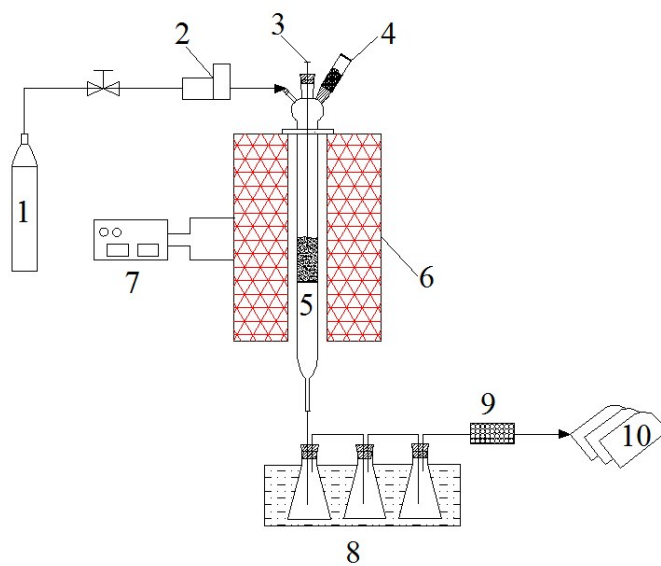
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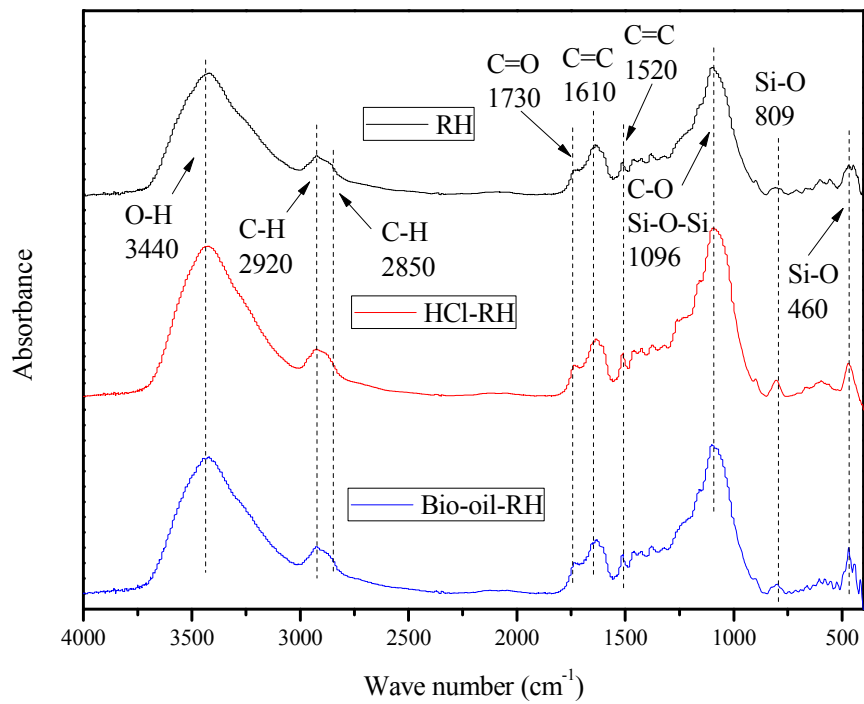
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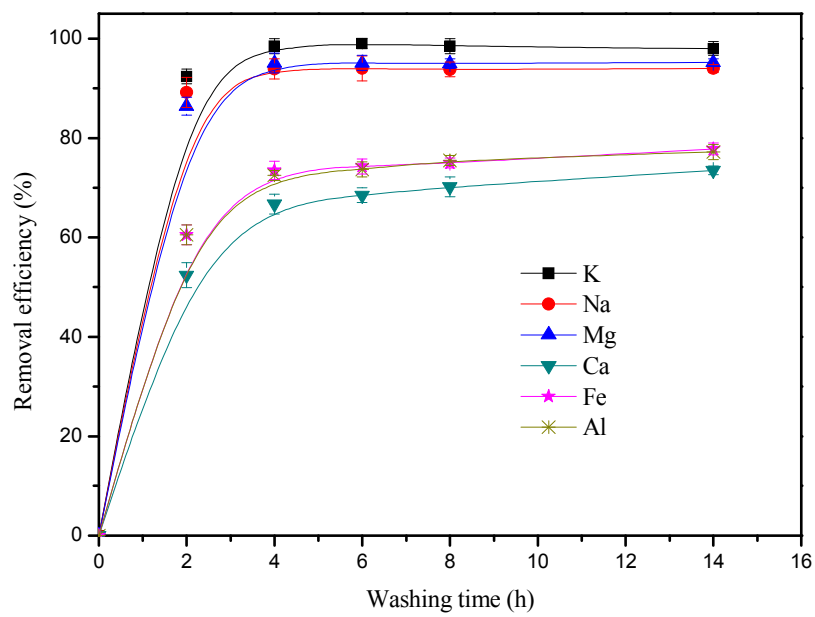
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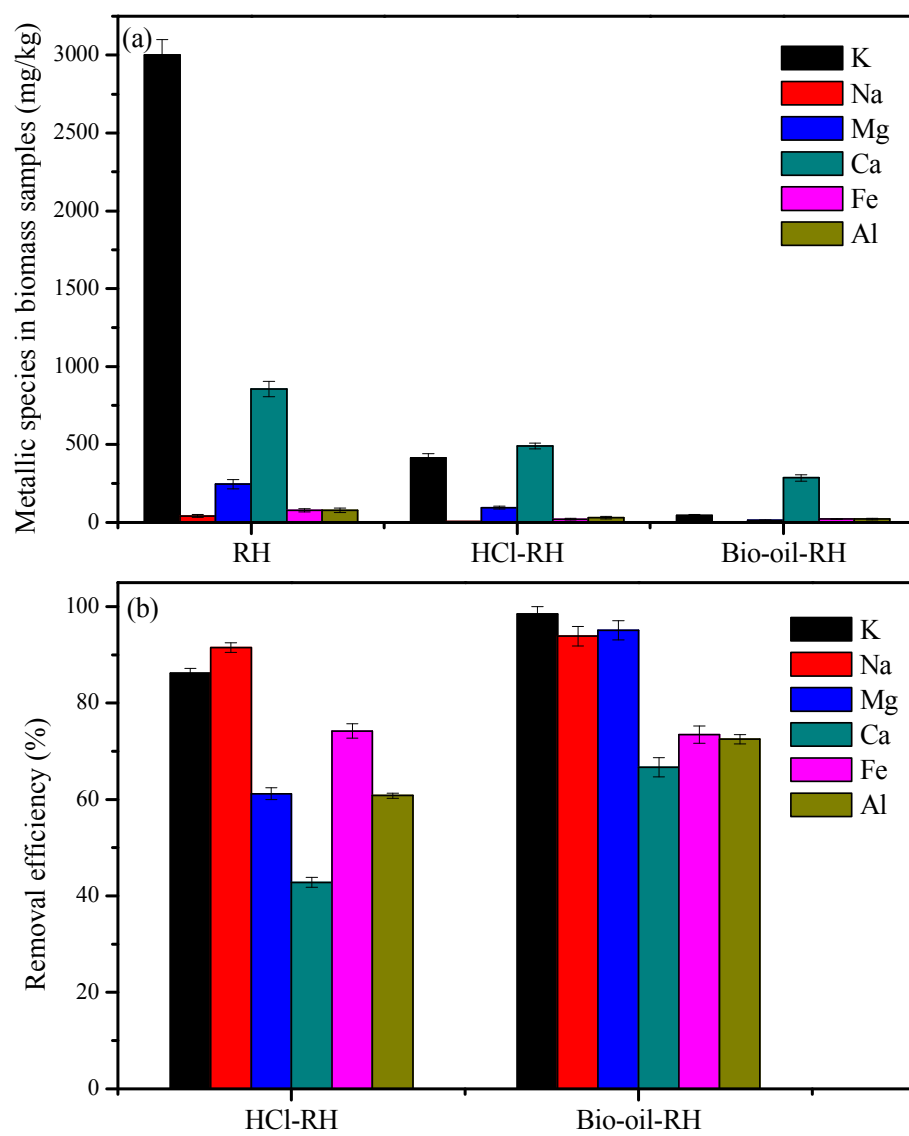
Fig. 5

Fig. 6

Fig. 7

This work demonstrates a new method that rice husk was converted into value added bio-based products such as bio-oil and biochar by washing pretreatment with light bio-oil followed by fast pyrolysis.