

# Upgrading of reed pyrolysis oil by catalytic esterification using solid acid catalyst generated from reed biochar

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## ABSTRACT

Pyrolysis is an effective way to convert aquatic plants into high-value products. The pyrolysis oil has high energy density but is difficult to utilize. In order to clean and economically convert the acids in pyrolysis oil into high grade esters, improving the quality of pyrolysis oil, this study chose seawater and freshwater reeds as raw materials, upgrading reed pyrolysis oil through catalytic esterification by reed biochar-based solid acid catalyst and comparing the catalytic effect of reed biochar-based solid acid catalysts with commercial 732 and NKC-9 solid acid catalysts. After analyzing the pyrolysis products of two kinds of reeds, seawater reed pyrolysis oil generated from 600°C (has the highest acid content) was chosen as raw oil to upgrade its quality, and biochar generated from 600°C and 700°C was chosen to produce catalysts. The acid content in upgraded oil was significantly reduced, and ester became the main component of upgraded oil. Among the six catalysts, 732-catalyzed upgraded oil had the highest ester content (21.97%). The 700°C freshwater reed biochar-based catalyst has comparable catalytic effect to that of NKC-9, the ester contents of their upgraded oil were 18.71% and 19.98%, respectively. Catalytic effects were proportional to surface sulfonic acid contents of the catalysts. Compared with raw pyrolysis oil, heat value of upgraded oil increased by 15.16%-76.54%, and viscosity decreased from 11.47Pa·s to about 3Pa·s. The commercial catalysts decreased the pH of upgraded oil to a lower value, but the reed biochar-based solid acid catalyst increased the pH value of upgraded oil to about 5, this was attributed to the fact that reed biochar-based solid acid catalyst has a superior thermal stability than that of the commercial catalysts, so that sulfonic acid group was not easily peeled off after being heated. The obtained results could provide a guidance for the relationship between biomass feedstocks, pyrolysis conditions, catalytic activity of biochar-based solid acid catalyst and upgrading effect of pyrolysis oil.

**Keywords:** reed, solid acid catalyst, pyrolysis oil, esterification, upgraded oil

## 1. INTRODUCTION

Reed cutting can improve the water environment. Pyrolysis can achieve quantitative reduction, cleanliness and high value conversion of reeds. Reed pyrolysis oil, as one of the important pyrolysis products, is not as good as fossil fuels because of its high acidity, low heating value, high corrosiveness, high viscosity and poor stability. The compositions of bio-oil are mainly including acids, ketones, aldehydes, esters, ethers, alcohols, phenols, as well as carbohydrates, and the other oxygenated organics. Considering stable oxygenated compounds themselves are good liquid fuels and can be added to fossil fuels, and oxygen in combustibles helps combustion [1]. Therefore, pyrolysis oil can be upgraded with simple oxygenates as target, and converting the organic acids which have strong corrosiveness and poor stability into a neutral, stable, high heating value ester by the principle of esterification reaction. The acid content of reed pyrolysis oil is as high as 35.33wt%, which is an ideal raw material for esterification. The esterification requires strong acid as a catalyst, this research choose a solid acid catalyst generated from reed biochar to study its catalytic esterification upgrading effect of reed pyrolysis oil, and select commercial 732 and NKC-9 type cation exchange resin for comparison.

## 2. MATERIALS AND METHODS

### 2.1 Raw materials

Seawater reed and freshwater reed were chosen as raw materials. Before pyrolysis, the reeds were exposed to the sun in a greenhouse for a week, then crushed and sieved to obtain particles smaller than 2 mm.

### 2.2 Experimental methods

#### 2.2.1 Preparation of catalysts

The catalysts were prepared by pyrolysis and sulfonation. The experimental conditions are shown in

Table 1. The obtained pyrolysis oil was refrigerated at 4°C before use. Reed biochar was milled into powders with a particle size of 1-2 mm, then mixed with 98% sulfate in a ratio of 1g:12ml. The sulfonation experiment was carried out in an oil bath capped with a temperature control device. A magnetic stirrer was used during sulfonation process. After sulfonation, the mixture was cooled to

room temperature and injected into deionized water, then stirred and filtered with a sand core funnel, the filter cake was washed repeatedly with deionized water at 80°C until the pH of filtrate was near neutral. The filter cake was broken and dried at 100°C for 24 h, then stored in a drying utensil before use.

Table 1 Preparation of reed biochar-based solid acid catalysts

		Pyrolysis experiment			Sulfonation experiment			
raw material	Temperature (°C)	pyrolysis condition	pyrolysis oil	biochar	sulfonation agent	Temperature (°C)	Time (h)	products (catalysts)
SWR <sup>1</sup>	500	carrier gas: N <sub>2</sub> flow rate: 80ml/min heating rate: 20°C/min residence time: 1h cool to room temperature	500SWO	500SWC	98% sulfate	—	—	—
	600		600SWO	600SWC		135	2	600SWS
	700		700SWO	700SWC		135	2	700SWS
FWR <sup>2</sup>	500	residence time: 1h cool to room temperature	500FWO	500FWC	98% sulfate	—	—	—
	600		600FWO	600FWC		135	2	600FWS
	700		700FWO	700FWC		135	2	700FWS

<sup>1</sup>. Reed grown in seawater. <sup>2</sup>. Reed grown in freshwater

### 2.2.2 Esterification experiment

Among 6 kinds of pyrolysis oil, 600SWO has the highest acid content (section 3.1), It is most suitable for being used as raw oil for esterification. The esterification

experimental condition is shown in Table 2. In order to clarify the catalytic effects of reed biochar-based catalysts, commercial solid acid catalysts named 732 and NKC-9 were used to compare with them.

Table 2 Experimental design of esterification

No.	Conditions of esterification	Catalysts	Upgraded oil
1		732 <sup>3</sup>	732E
2	600SWO <sup>1</sup> : ethanol <sup>2</sup> (V: V) =1:2	commercial	NKC-9 <sup>4</sup>
3	reaction temperature: 70°C		600SWS
4	reaction time: 2h		700SWS
5	amount of catalyst: 10% mass of 600SWO	reed biochar-based	600FWS
6			700FWS

<sup>1</sup>. Seawater reed pyrolysis oil generated from 600°C.

<sup>3</sup>. 732 type cation exchange resin.

<sup>2</sup>. Absolute ethanol.

<sup>4</sup>. NKC-9 type macropores cation exchange resin.

## 3. RESULTS AND DISCUSSION

### 3.1 Characteristics of reed pyrolysis oil

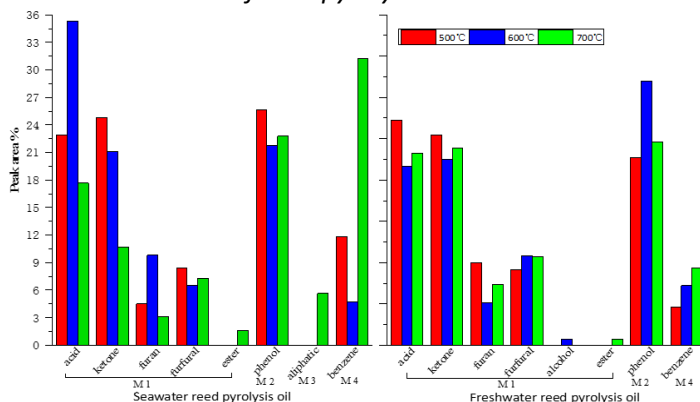


Figure 1 Components and content of seawater reed pyrolysis oil and freshwater reed pyrolysis oil

The components of pyrolysis oil generated from two kinds of reed and three pyrolysis temperatures were

shown in Fig.1. Dividing pyrolysis oil into four categories, M1: acid, ketone, furan, furfural, ester, alcohol; M2: phenol; M3: aliphatic; M4: benzene. For SWO, 500SWO and 600SWO mainly have M1 and M2. The acid (mainly acetic acid) content in 600SWO was the highest (35.33%), which was most suitable for esterification. In 700SWO, the M1 content reduced and M4 content greatly increased, in addition, M3 was new appeared, that was due to the polymerization of small molecules in pyrolysis oil to generate M3 and M4 which were more stable. For FWO, with pyrolysis temperature increased, M1 content decreased and M4 content increased, but in 700FWO, M1 content showed a small increase. The characteristics of pyrolysis oil were related to the precipitation characteristics of AAEMs with temperature in two kinds of reeds. Table 3 shows the main elements in two kinds of reed. The melting point of chlorides is much lower than that of other salts. During pyrolysis process, the pressure inside biochar increased, chlorides

was melted at a lower temperature (<700°C), then migrated with the volatiles [2]. Research by Patwardhan et al. [3] showed that AAEMs can promote the secondary

cleavage of macromolecular compounds and other reactions that compete with the depolymerization, thereby 600SWO has the highest content of M1.

Table 3 The content of elements in raw materials (%)

Raw materials	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZnO	TiO <sub>2</sub>	Cl	SO <sub>3</sub>	SiO <sub>2</sub>
SWR	1.21	0.14	1.08	0.11	0.07	0.41	0.02	0.02	2.15	2.17	10.50
FWR	1.05	0.07	2.49	0.14	0.11	0.94	0.03	0.13	1.39	1.37	10.30

### 3.2 Characteristics of reed biochar-based solid acid catalyst

#### 3.2.1 Surface functional groups

Surface functional groups of reed biochar and solid acid catalysts were characterized by FTIR, the results were shown in Fig.2. Compared (b) with (a), the symmetric stretching vibration (1710cm<sup>-1</sup>) of S=O and the

asymmetric stretching vibration (1037cm<sup>-1</sup>) of S-O in sulfonic acid group appeared, indicating that the sulfonic acid groups were successfully loaded on the surface of reed biochar after sulfonation. The broad band at 2,700-2,900 cm<sup>-1</sup> was assigned to an overtone (Fermi resonance) of the bending mode of -OH...O= linked by a strong hydrogen bond, which suggests that some SO<sub>3</sub>H groups are in close proximity to each other[4].

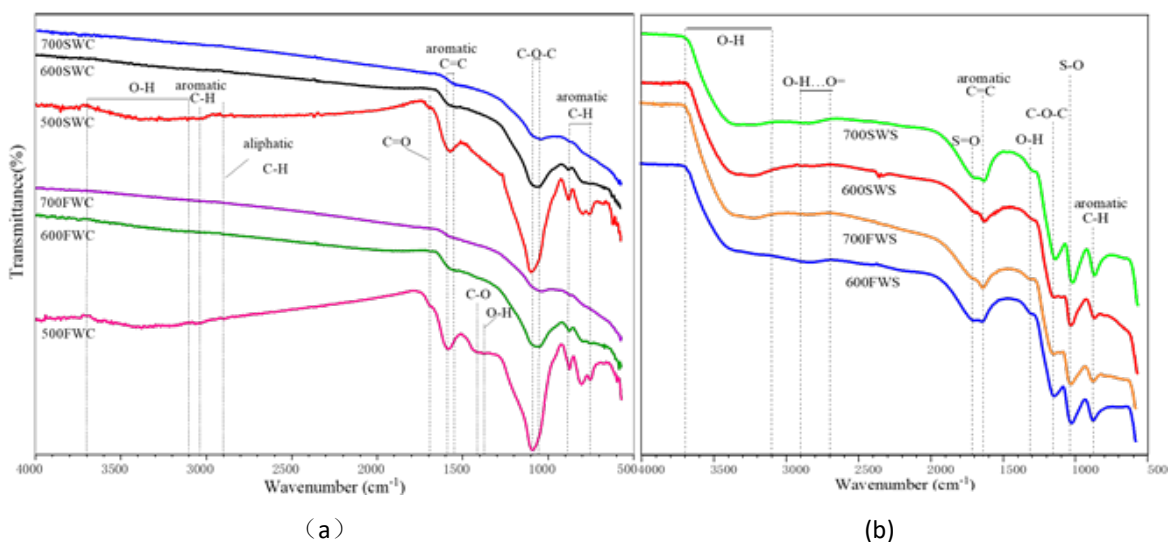


Figure 2 Surface functional groups of reed biochar (a) and reed biochar-based solid acid catalysts (b)

#### 3.2.2 Surface acid content of solid acid catalysts

The FTIR analysis (Fig. 2) showed that the solid acid catalysts contain not only strongly acidic -SO<sub>3</sub>H functional groups but also weakly acidic groups. The amount of strong acid, weak acid and total acids contain in the solid acid catalysts are shown in Table 4.

Table 4 The amount of surface acids contained in solid acid catalysts (mmol/g)

Catalyst	Sulfonic acid	Weak acid	Total acid
732	1.82	—	1.82
NKC-9	1.02	—	1.04
600SWS	0.48	0.51	1.35
700SWS	0.45	0.97	1.39
600FWS	0.66	0.77	1.49
700FWS	0.99	0.08	0.98

The sulfonic acid content of commercial catalysts is higher than that of reed biochar-based solid acid catalysts. For SWS, the sulfonic acid content of 600SWS is higher than that of 700SWS, while total acid content is comparable to that of 700SWS. For FWS, the sulfonic acid content of 600FWS is lower than that of 700FWS, but weak acid content and total acid content of 600FWS are both higher than that of 700FWS.

#### 3.2.3 Thermal stability of reed biochar-based solid acid catalyst

The thermal stability of reed biochar-based solid acid catalysts was tested by thermogravimetric analyzer, the results are shown in Fig.3. The four kinds of reed biochar had a peak of weight loss when temperature was raised to 100°C, which is due to moisture removal. However, the dehydration of reed biochar-based solid

acid catalysts occurred at a higher temperature, mainly because  $-SO_3H$  is hydrophilic and has an adsorption force on water molecules, which made water molecules in catalysts have more adhesion. Therefore, a higher temperature is required to remove it.

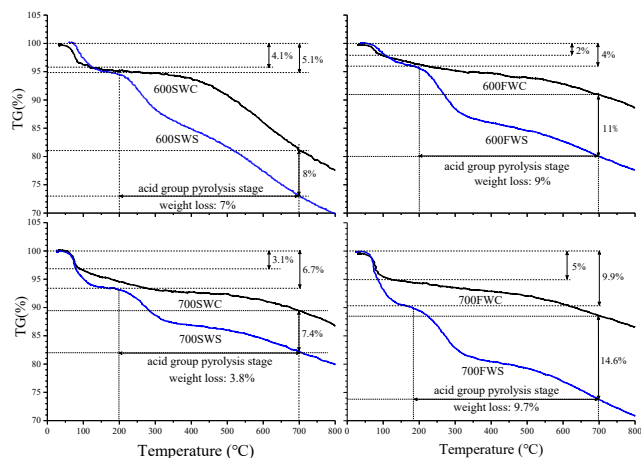


Figure 3 Thermogravimetric curve of reed biochar and reed biochar-based solid acid catalysts

Reed biochar-based solid acid catalysts showed a second peak of weight loss after 200°C, which was caused by the decomposition of  $-SO_3H$ . 600SWS, 700SWS, 600FWS and 700FWS had a more 7%, 3.8%, 9% and 9.7% weight loss than their biochar which are basically proportional to sulfonic acid content of themselves (Table 4). This indicates that the reed biochar-based solid acid catalysts had good thermal stability, and did not decompose below 200°C. When the temperature increased to a higher temperature, the  $-SO_3H$  will gradually desorb in the form of  $SO_2$ [5].

### 3.3 Catalytic esterification effect of reed pyrolysis oil

Table 5 shows characteristics of 600SWO and the upgraded oil. After esterification, the target product ester (mainly ethyl acetate) became the main component of upgraded oil. The order of catalytic effect is: 732>NKC-9>700FWS>600FWS>600SWS>700SWS, the catalytic effect of 700FWS was comparable to that of NKC-9.

Table 5 Characteristics of 600SWO and upgraded oil

Catalysts	Ester content of upgraded oil (%)	pH value		Heat value (MJ/kg)		Viscosity (30°C, Pa·s)		
		600SWO	upgraded oil	600SWO	absolute ethanol	upgraded oil	600SWO	upgraded oil
Commercial	732	21.97	3.41±0.02			23.44±0.02		2.84±0.03
	NKC-9	19.98	2.95±0.03			25.51±0.02		3.08±0.02
Reed biochar-based	600SWS	14.25	5.42±0.01	14.45±0.33	17.38±0.03	23.93±0.03	11.47±0.15	3.34±0.02
	700SWS	6.62	4.81±0.02			16.64±0.05		3.01±0.03
	600FWS	15.69	5.08±0.02			19.36±0.03		2.88±0.01
	700FWS	18.71	5.10±0.01			24.66±0.06		2.86±0.02
Heavy fuel oil		—	—	40.5		0.38		—

## 4. CONCLUSION

The quality of reed pyrolysis oil can be effectively improved by catalytic esterification through reed biochar-based solid acid catalyst. The upgraded oil is a black liquid that is uniform, flowable and has aromatic odor. Considering both catalytic effect, economy and environmental friendliness, 700FWS is the best choice for upgrading pyrolysis oil. According to the obtained results, considering the products characteristics and upgrading effect of pyrolysis oil, it is recommended that pyrolysis temperature  $\leq 600^\circ C$  when choose biomass grow in seawater or saline-alkali as pyrolysis raw materials, and pyrolysis temperature  $\geq 700^\circ C$  when choose biomass grow in an ordinary environment.

## ACKNOWLEDGEMENT

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