

## Phenols Production from Online Catalytic Conversion of Corn Stalk Pyrolysis Vapors using Char *in-situ*

Yunchao Li,<sup>a</sup> Xianhua Wang,<sup>b,\*</sup> Huawei Song,<sup>a</sup> Jingai Shao,<sup>b</sup> Hongtao Ma,<sup>a</sup> and Hanping Chen<sup>b</sup>

Char *in-situ* (char<sub>is</sub>) obtained from corn stalk pyrolysis was evaluated as a catalyst to upgrade corn stalk pyrolysis vapors. A catalyst evaluation device was introduced to conduct the experiments. The effects of reaction temperature and char<sub>is</sub> dose on catalytic performances in biomass pyrolysis were evaluated. The results showed that the char *in-situ* had a remarkable effect on the pyrolysis products. Under the action of char<sub>is</sub>, the primary compounds of pyrolysis vapors were catalytically converted into phenolic products, such as phenol and 4-ethyl-phenol, while the acetic acid content was evidently reduced. The product selectivity was not dependent on the polar functional groups on the char<sub>is</sub>'s surface according to the Fourier transform infrared (FTIR) results, but might have been dependent on the mesoporous structure and the basicity sites of the char<sub>is</sub> as well as the metallic species in the char<sub>is</sub>. A possible reaction mechanism for phenols production and acetic acid inhibition was proposed.

*Keywords:* In-situ upgrading; Pyrolysis; Char; Bio-oil; Phenols

*Contact information:* a: Huadian Electric Power Research Institute Co., Ltd., Hangzhou 310030, China; b: State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China; \*Corresponding author: wangxianhua@hust.edu.cn

### INTRODUCTION

Due to the shortage of fossil fuels and increasing environmental concern, renewable energy has attracted great attention in the past few decades. Lignocellulosic biomass, due to its renewability, low cost, wide availability, and CO<sub>2</sub> neutral features, is being studied as a promising alternative energy source. Pyrolysis is considered as an efficient technology to convert biomass into liquid fuel (bio-oil), solid char, and non-condensable gas (Papari *et al.* 2017). Among them, bio-oil has the potential to replace fossil fuels and can also be used as a feedstock for valuable chemical production (Elkasabi *et al.* 2015). Actually, many value-added chemicals exist in bio-oils, such as levoglucosan (LG), furfural, phenolic products, and more. However, currently, it is uneconomical to recover these valuable compounds from bio-oils due to their low concentrations (Ren *et al.* 2017). Through specific pre-treatment or catalytic pyrolysis of biomass, previous studies have been developed to upgrade bio-oil into fuels or chemicals. Although it may result in the formation of additional water or coke, or decrease the yield of bio-oil, the *in-situ* catalytic cracking of pyrolysis vapors is efficient to upgrade bio-oil (Lødeng *et al.* 2013). By using appropriate catalysts, the production of target compounds will be promoted and the undesirable compounds will be suppressed.

In previous studies, the traditional zeolite catalysts have been extensively studied, for example HY, HZSM-5, *etc.* (Sharma and Bakhshi 1993; Qi *et al.* 2007; Lu *et al.* 2010a; Stefanidis *et al.* 2011). The zeolite catalysts were found to effectively transform the

oxygenated compounds to the low oxygen-containing organic substances, such as hydrocarbons. However, the zeolite catalysts are easily inactivated because of the coke deposition. The yield of liquid would be decreased, and the polycyclic aromatic hydrocarbons could abundantly form (Lu *et al.* 2010a). In recent studies, mesoporous catalysts, such as SBA-15, Al-MCM-41, and others, have been used for upgrading the biomass pyrolysis vapors because of their specific porosity and acidic nature (Adam *et al.* 2006; Iliopoulou *et al.* 2007). However, compared to the zeolite catalysts, the mesoporous catalysts are hydrothermally unstable and have a high production cost, thus inhibiting their applications. In addition, most of them may suffer deactivation caused by coke deposition on their surfaces (Mortensen *et al.* 2011).

Pyrolysis char is a by-product from biomass pyrolysis. It has a low cost and a porous structure, containing some alkali metallic species. Due to its special physical and chemical properties, pyrolytic char is regarded as a potential catalyst (Bartocci *et al.* 2018). Sun *et al.* (2011) used pine wood char to crack the tar and found it active catalytically for the tar cracking at 500 °C to 600 °C. Keown *et al.* (2008) investigated the influence of char-volatile interactions on the alkali and alkaline earth metals (AAEM) species' volatilization during the biomass gasification process. However, there has been a lack of studies that focus on the online catalytic conversion of biomass vapors using char *in-situ* to obtain high quality bio-oil.

In this paper, the char is used as a catalyst for *in-situ* upgrading of pyrolysis vapors of biomass. The corn stalk is selected as the experimental sample. The effects of reaction temperature and char dose on catalytic performances in biomass pyrolysis are evaluated. The ultimate products are analyzed and the possible reaction mechanism is proposed. It should be noted that although the characteristics of the char would be slightly changed in the reaction, the char is still defined as a catalyst in this paper.

## EXPERIMENTAL

### Materials

The corn stalk (Caidian Farm, Wuhan, China), with a particle size from 40-mesh to 200-mesh, was used as the pyrolysis feedstock in a catalyst evaluation device (WFS-3070; Xianquan Co., Tianjin, China), as shown in Fig. 1. The properties of the corn stalk are given in Table 1. The char *in-situ* (char<sub>is</sub>) was also pre-prepared in the device by pyrolyzing the corn stalk at different temperatures (400 °C to 600 °C). The pyrolysis residence time for char<sub>is</sub> preparation was 90 min to ensure that the corn stalk was completely decomposed and that no secondary cracking would occur in the following catalytic process.

**Table 1.** Properties of Corn Stalk

Elemental analysis (wt%, ar)					Proximate Analysis (wt%, ar)				LHV (MJ/kg)
C	H	N	S	O*	M	V	A	FC	
41.43	5.33	1.42	0.11	37.76	3.45	73.62	10.50	12.43	16.33
* Oxygen content is calculated by the difference									

### Pyrolysis experiments

For each pyrolysis experiment, approximately 4.0 g of corn stalk sample was loaded into the left tube (the pyrolysis reactor, with a length of 630 mm and an inside diameter of 24 mm) with loose quartz wool packing. The char<sub>is</sub> was kept in the right tube (the catalytic reactor, with a length of 450 mm and an inside diameter of 18 mm) which was pre-heated to the set temperature (the same temperature as the carbonization temperature). The corn stalk was then heated from room temperature to the pre-set temperature (the same as the temperature of the pyrolysis reactor) with a heating rate of 20 °C/min. All of the pipes were insulated, and the inner atmosphere was nitrogen gas with a flow rate of 200 mL/min. The pyrolysis vapors then passed through the char<sub>is</sub>. The mass ratio of the char<sub>is</sub> to corn stalk was 0.125 (0.5 g) and 0.25 (1 g), respectively. After leaving the reactor, the pyrolysis vapors were condensed in an ice-water condenser operating at approximately 0 °C. The liquid products (bio-oil) were quantitatively weighed and collected using acetone as the solvent. The char yield in this paper was defined as the solid residue (abbreviated as char<sub>sr</sub>) in the pyrolysis reactor, which was collected and weighed. The reacted char (char<sub>is</sub>) in the catalytic reactor was also weighed. The yield of the uncondensable gas was calculated by the difference. For comparison, tests without char<sub>is</sub> in the catalytic reactor were also performed. It should be noted that the residence time of the pyrolyzer was also kept as 90 min to make sure the reaction was complete. In contrast, the gas analyzer used in the experiment had a certain lag because of the gas residence time in the condensation system. All of the experiments were conducted twice to guarantee the results were reproducible.

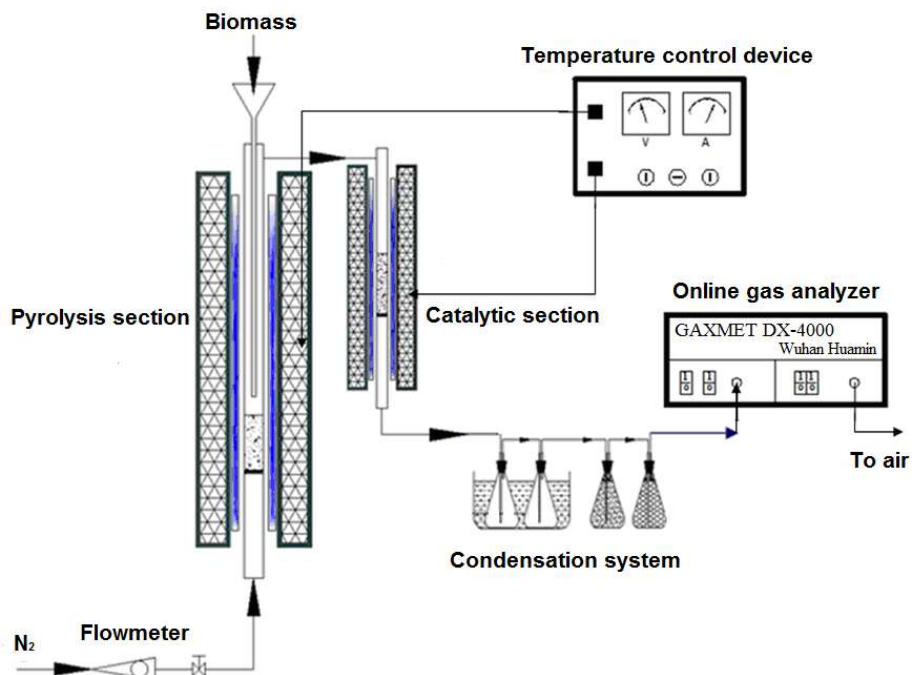


Fig. 1. Schematic diagram of the catalyst evaluation device

## Methods

### Characterization of the products

The main components of bio-oil were determined by gas chromatography-mass spectroscopy (GC-MS, Agilent 7890A/5975C; Agilent Technologies Inc., Santa Clara, CA, USA). The capillary column was HP-5-MS (30 m × 0.25 mm × 0.25 μm). The

temperature of GC oven was first 40 °C maintained for 0.5 min and then raised to 270 °C for 5 min at a rate of 5 °C/min. The temperature of the injector was 280 °C with a split ratio of 50:1. After 2 min of solvent delay, the sample was injected into the ion source of a Hewlett-Packard model 5975 series mass-selective detector (Agilent Technologies Inc., Santa Clara, CA, USA) and scanned over a range of 30 m/z to 500 m/z. The software MSD Chemstation (Agilent Technologies Inc., E.01.00.237, Santa Clara, CA, USA) was used to identify the compounds based on the retention time. Other instrument settings and operating parameters can be found in the authors' previous study (Li *et al.* 2016). The organic functional groups of the char<sub>is</sub> before and after reactions were detected in a VERTEX 70 spectrophotometer (Bruker, Ettlingen, Germany) (Li *et al.* 2014). The surface area of the char<sub>is</sub> was measured by nitrogen adsorption (Micromeritics, Norcross, GA, USA), and the basicity of the char<sub>is</sub> was determined by Boehm titration (Li *et al.* 2013, 2014). The gas components were determined by an on-line infrared gas analyzer with a thermal conductivity detector (TCD) for H<sub>2</sub> (Huamin, Wuhan, China), and the relative content of the different components was calculated from their peak areas.

## RESULTS AND DISCUSSION

### Product-distribution Properties

The yield distributions of bio-oil, char<sub>sr</sub>, and uncondensable gas from corn-stalk pyrolysis at the temperatures between 400 °C and 600 °C, are shown in Fig. 2. The horizontal axis of Fig. 2 represents the experimental conditions. For instance, “400” means the pyrolysis temperature was 400 °C without char present; “400-1.0” means that the pyrolysis temperature was 400 °C and the char dose was 1.0 g. As shown, the yield of bio-oil increased with increased temperature from 400 °C to 500 °C, and reached its maximum value (37.1 wt%) at 550 °C. The char<sub>sr</sub> yield was reduced as the temperatures increased. Higher temperatures increased the gaseous product yield.

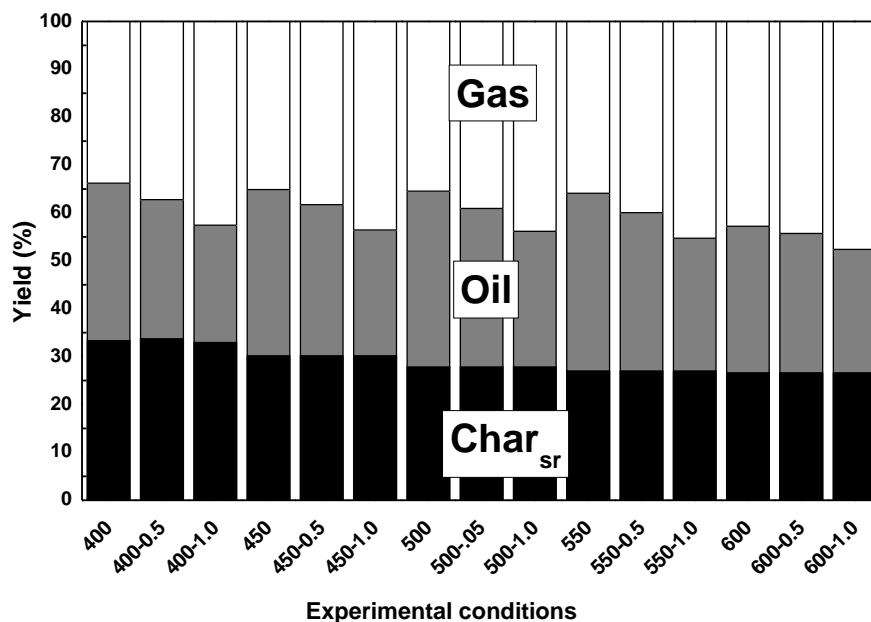


Fig. 2. Product-distribution from corn stalk on-line catalytic pyrolysis

After interacting with the char<sub>is</sub>, the yield of the bio-oil declined, and as the char<sub>is</sub> dose increased, the bio-oil yield further decreased. For example, the yield of the bio-oil was 37.1 wt% at 550 °C, and it decreased from 33.05 wt% to 27.7 wt% as the char<sub>is</sub> dose was 0.5 g and 1.0 g, respectively. This decrease might have been due to the decomposition of bio-oil promoted by the char<sub>is</sub>, polymerization to form chars, or adsorption into the char<sub>is</sub> pores. The gas yield also increased with the char<sub>is</sub> present, and the increase might have been caused by the secondary cracking reaction.

**Table 2.** Composition of Bio-oil Determined by GC/MS at 550 °C

No.	Retention Time (min)	Compound	Area Percentage (%)		
			Original	Char <sub>is</sub> = 0.5 g	Char <sub>is</sub> = 1.0 g
1	1.807	Acetic acid	31.42	21.73	17.19
2	1.896	Hydroxyacetone	6.07	1.97	--
3	2.573	Propionic acid	1.54	1.14	--
4	2.987	Hydroxybutanone	0.53	--	--
5	3.292	Tetrahydrofuran alcohol	0.57	--	--
6	3.323	Other	--	0.87	1.52
7	3.583	Other	--	--	2.51
8	4.628	2-Furanylmethanol	2.20	0.96	--
9	4.879	Other	1.70	--	--
10	4.925	Other	--	0.56	0.97
11	5.872	Other	1.85	1.83	--
12	7.837	Phenol	7.77	8.82	15.96
13	8.331	Other	1.08	1.06	--
14	8.376	Other	--	--	1.39
15	9.015	Hydroxy-3-methylcyclopentenone	1.93	1.20	--
16	9.205	2,3- Dimethylcyclopentenone	0.68	0.96	--
17	9.874	2- Methylphenol	2.71	3.21	4.85
18	10.493	4- Methylphenol	2.57	4.92	6.16
19	10.66	3- Methylphenol	0.93	--	--
20	11.046	Other	--	0.52	--
21	10.932	Other	1.39	--	--
22	11.621	3-Ethyl-2-hydroxycyclopentenone	0.62	--	--
23	12.516	2,3- Dimethylphenol	0.83	1.56	--
24	12.974	4- Ethylphenol	5.53	15.02	25.50
25	13.319	3,4- Dimethylphenol	--	1.11	--
26	14.16	Dehydrated- $\alpha$ -D-glucopyranose	1.35	1.52	2.68
27	14.306	1,2- Hydroquinone	1.59	2.35	--
28	14.472	2,3-Dihydrobenzofuran	17.71	11.42	13.92
29	14.602	Other	--	3.67	--
30	14.87	2-Ethyl-6-methylphenol	1.85	3.78	3.07
31	15.482	4- Ethylphenol	--	1.12	--
32	15.995	Other	--	0.49	--
33	16.162	Other	0.73	0.97	--
34	16.98	4-Methyl 1,2-benzenediol	1.03	1.41	--
35	17.112	3-Methyl 1,2-benzenediol	0.66	1.65	--
36	17.552	3-Methyl 1,2-benzenediol	--	0.27	--
37	19.833	4,5-Dimethyl-1,2-benzenediol	--	1.47	--
38	25.729	Phenanthrene	1.75	1.66	4.27
39	27.008	N- Palmitic acid	1.07	0.77	--
40	27.976	<i>trans</i> -13-Octadecenoic acid	0.35	--	--

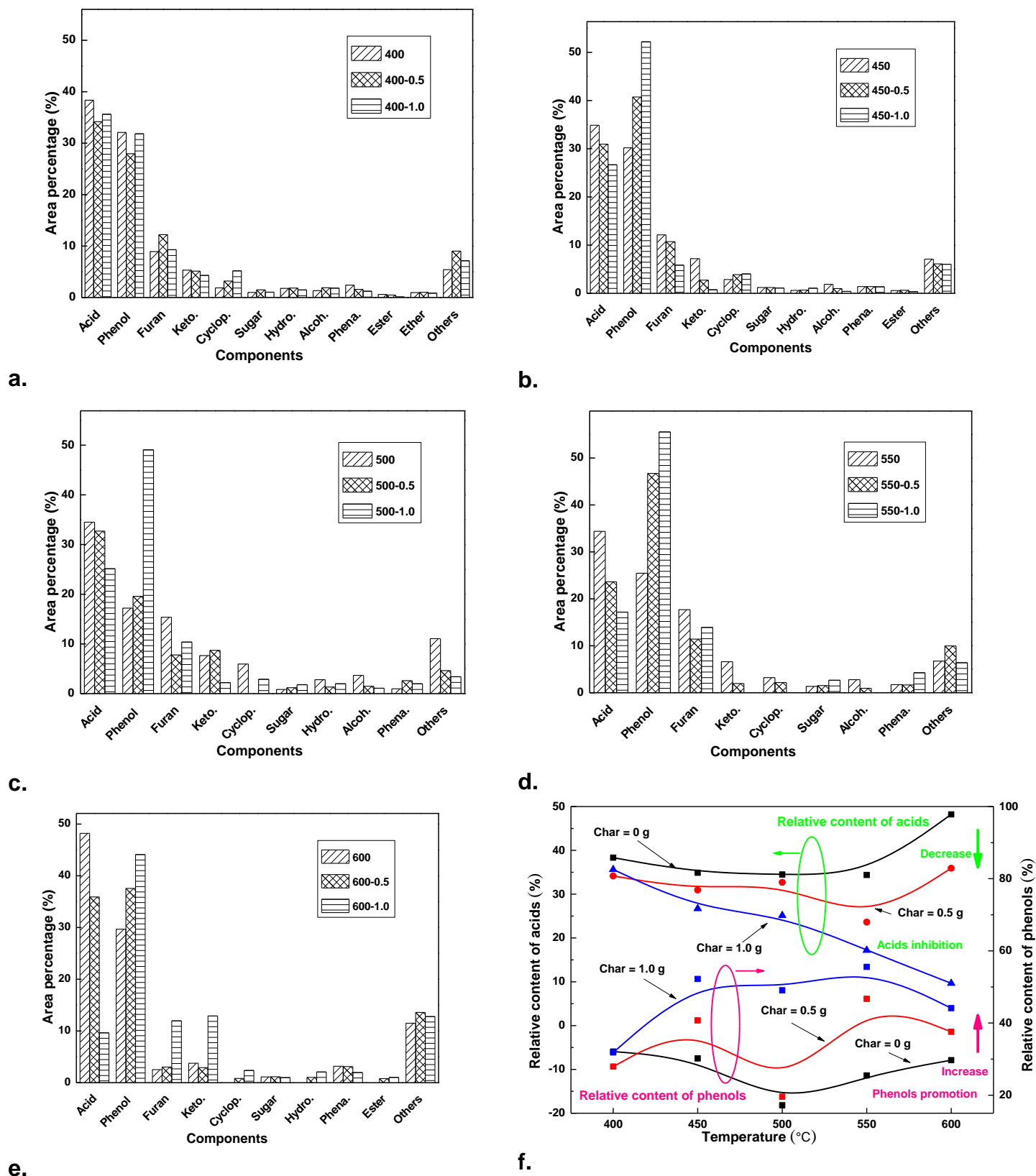
## Bio-oil Properties

Table 2 lists the composition of bio-oil at 550 °C. As is known, the peak area percentage of the GC/MS chromatogram is considered linear with its relative compound content (Lu *et al.* 2010b). As shown, the chemical compounds of the original bio-oil without char<sub>is</sub> mainly consisted of acetic acid (31.42%, the peak area percentage), 2,3-dihydrobenzofuran (17.71%), phenol (7.77%), and hydroxyacetone (6.07%), with a small amount of dehydrated sugar (1.35%). Acetic acid was the major component in the original bio-oil. After interacting with the char<sub>is</sub>, the composition of bio-oil was notably changed. The acetic acid content was remarkably reduced from 21.73% to 17.19% when the char<sub>is</sub> dose changed from 0.5 g to 1.0 g. The content of 2,3-dihydrobenzofuran was also remarkably reduced. Simultaneously, the phenol increased from 7.77%, without char<sub>is</sub> present, to 8.82% and 15.96% with char<sub>is</sub> doses of 0.5 g and 1.0 g, respectively. The catalytic mechanism was discussed in the following sections.

To clearly show the change of compositions, the bio-oil components detected by GC/MS were classified into twelve groups (acids, phenols, furan, ketones, cyclopentenone, sugars, hydrocarbons, alcohols, phenanthrene, esters, ethers, and other compounds), as shown in Fig. 3. The highest relative content of phenols was obtained at 550 °C with a char<sub>is</sub> dose of 1.0 g, and the peak area percentage could reach up to 55.6%, while it was only 25.5% without catalytic process. The peak area of the acids also declined from 34.4% to 23.6% (0.5 g) and 17.2% (1 g), respectively. The char<sub>is</sub> reduced the formation of acids and promoted the phenol production. The phenols' selectivity increased as the char<sub>is</sub>-to-biomass ratio increased (Fig. 3f). Lu *et al.* used a NiO-catalyst and found that the content of phenol increased from 26.5% to 32.6% (peak area percentage) after catalytic reaction. The NiO-catalyst was thought to be promoting the depolymerization of lignin from the phenolic compounds (Le *et al.* 2010b). Adam *et al.* (2006) used a transition metal modified catalyst and found that the phenols yield was improved. Lu *et al.* also used the Pd/CeTiO<sub>2</sub> catalyst and found the peak area percentage of the phenols obviously increased, which indicated that the Pd incorporation would improve the cracking activity for lignin pyrolysis (Lu *et al.* 2010a). Sun *et al.* (2011) used pine wood char for tar decomposition and found that the carboxylic acids, furans, *etc.* substantially decreased with the phenols' increase. These results were similar to what the authors had achieved. As is known, the acids present in the bio-oil have a negative effect on the property of bio-oil. Thus, the reduction of its content is beneficial to bio-oil quality. Phenols are valuable chemicals that are widely used in resin production. Therefore, the catalyzed bio-oil may be used as a promising raw material for phenol recovery. Other organic components were detected as well, but in very low concentrations, and thus were not discussed further. As the char<sub>is</sub> achieved its best catalytic activity at 550 °C, the temperature of 550 °C was chosen in the following discussion.

## Properties of Gaseous Product

The gas compositions before and after char<sub>is</sub> catalysis at 550 °C are shown in Fig. 4. The major components in the gas phase were CO<sub>2</sub> (7857.1, peak area, relative content) and CO (6022.1), with small amounts of CH<sub>4</sub> (2459.1) and H<sub>2</sub> (435.5). As shown, the char<sub>is</sub> intensely facilitated the decomposition of pyrolysis vapors to gases in the forms of CO, CO<sub>2</sub>, *etc.*, and it was beneficial for the production of hydrogen and methane. After catalysis, the relative contents of CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub> were 12879.3, 8955.6, 4176.6, and 1372.2, respectively, with the char<sub>is</sub> dose of 1.0 g at 550 °C.



**Fig. 3.** Summary of classification of bio-oil components before and after char<sub>is</sub> catalysis (400 °C to 600 °C)

The production of CH<sub>4</sub> and H<sub>2</sub> in the catalytic pyrolysis might be attributed to the catalytic cracking of polysaccharide (Mante and Agblevor 2011). In the pore channel of char<sub>is</sub>, the vapors might have undergone a series of dehydrogenation, decarboxylation, decarbonylation, dehydration, and isomerization reactions that led to the formation of the phenolic substances and the small molecule gases. The gasification reaction or secondary cracking of charcoal might occur simultaneously, which resulted in the enhancement of the gas yield.

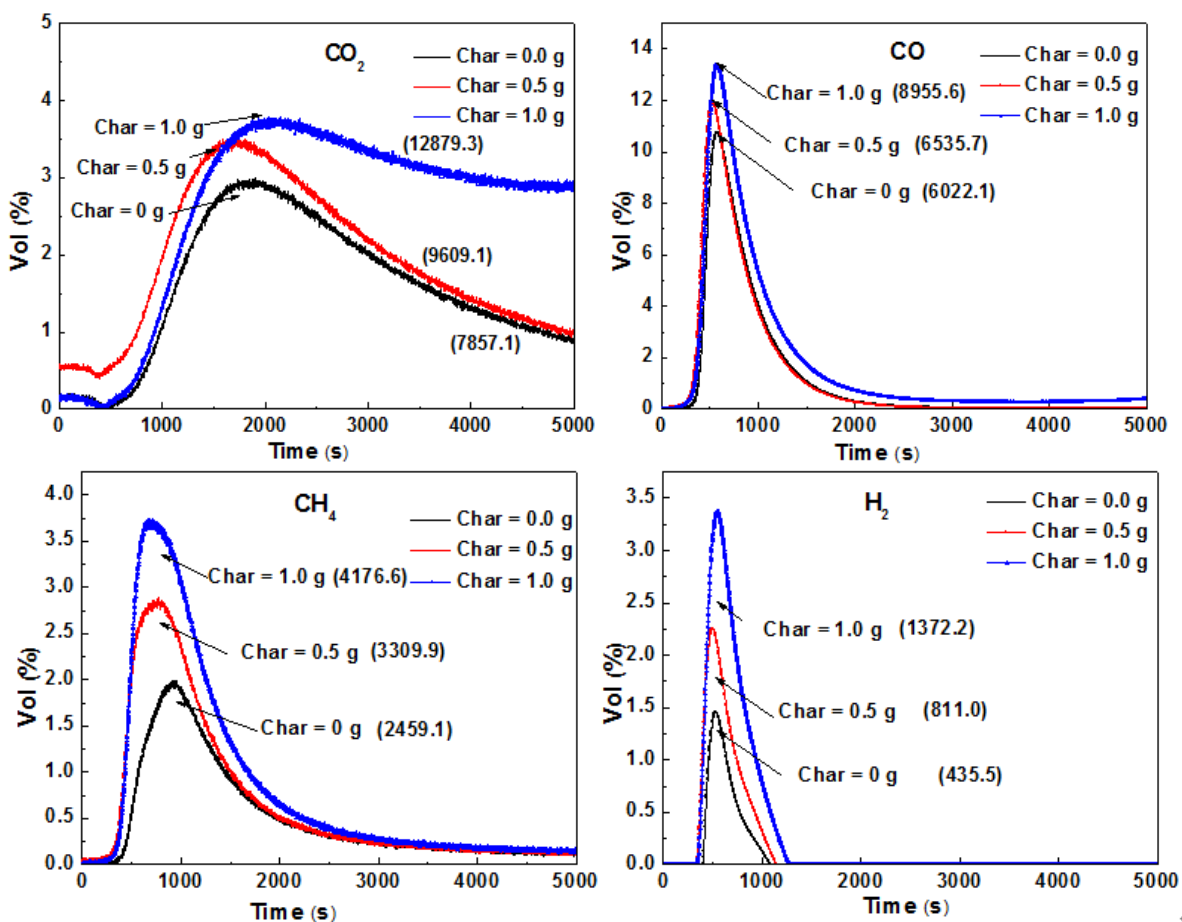


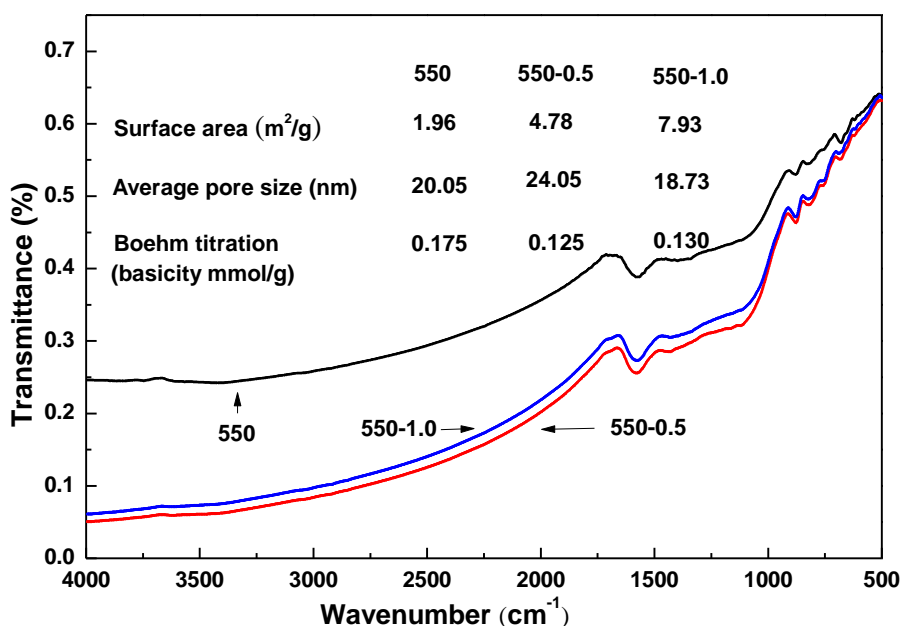
Fig. 4. The gas released under different pyrolysis conditions

### Properties of Solid Chars

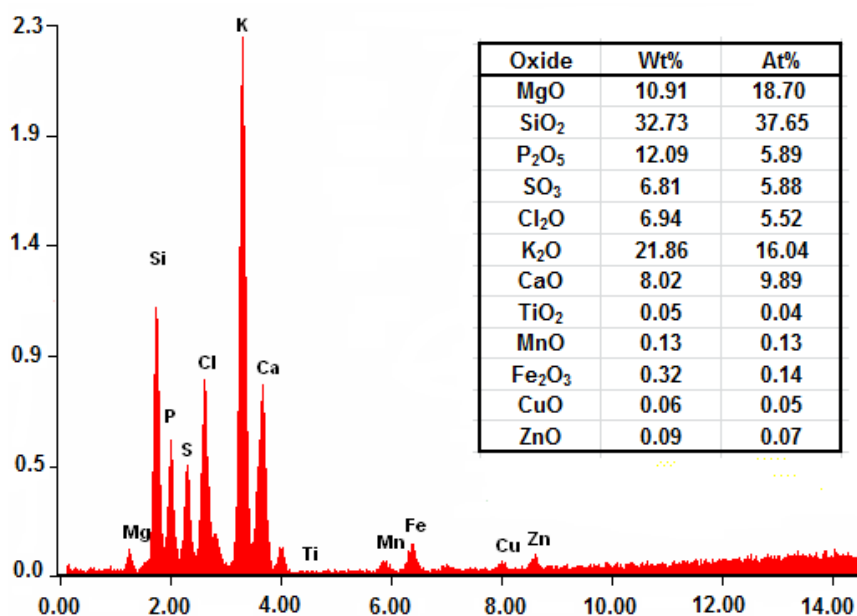
The char<sub>is</sub> in the catalytic reactor was weighed, and the result showed that the amount of the char<sub>is</sub> was not changed remarkably. This might have been due to the combined effect of the secondary cracking reaction (decreasing weight) and secondary coke forming or bio-oil adsorption (increasing weight). Figure 5 shows the infrared spectra, as well as the pore size and surface area of the chars before and after catalytic reaction. As shown, the polar functional groups on the surface of char<sub>is</sub> were not obviously changed. The surface area of original char<sub>is</sub> was small (1.96 m<sup>2</sup>/g), with an average pore size of 20.0 nm. The surface area of the char<sub>is</sub> increased after catalysis (4.78 m<sup>2</sup>/g to 7.93 m<sup>2</sup>/g), which might have been due to further evolution of the char<sub>is</sub> pore structures with prolonged residence time. Simultaneously, the vapors might also have been covered on the char<sub>is</sub> surface so that some pores were clogged. The increased surface area of the char<sub>is</sub> indicated that the pore development was the main process. The average pore size was not changed



noticeably after catalysis, and was mainly consisted of mesopores. The presence of the mesopores might have provided a reaction channel during the catalytic reactions. The Boehm titration result showed that the basicity of char<sub>is</sub> decreased (from 0.175 mmol/g to 0.125 mmol/g and to 0.130 mmol/g) after interacting with the vapors. The ash composition revealed that the main element in char<sub>is</sub> was K, followed by Si, Cl, and Ca. Perhaps these metallic species played an important role in the catalytic reaction. Keown *et al.* (2008) confirmed that the presence of alkali and alkaline earth metals in the char affected the char's activity and selectivity. Further experiments will be conducted to confirm the effects of these alkali metals and alkaline earth metals.



a

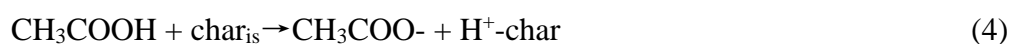


b

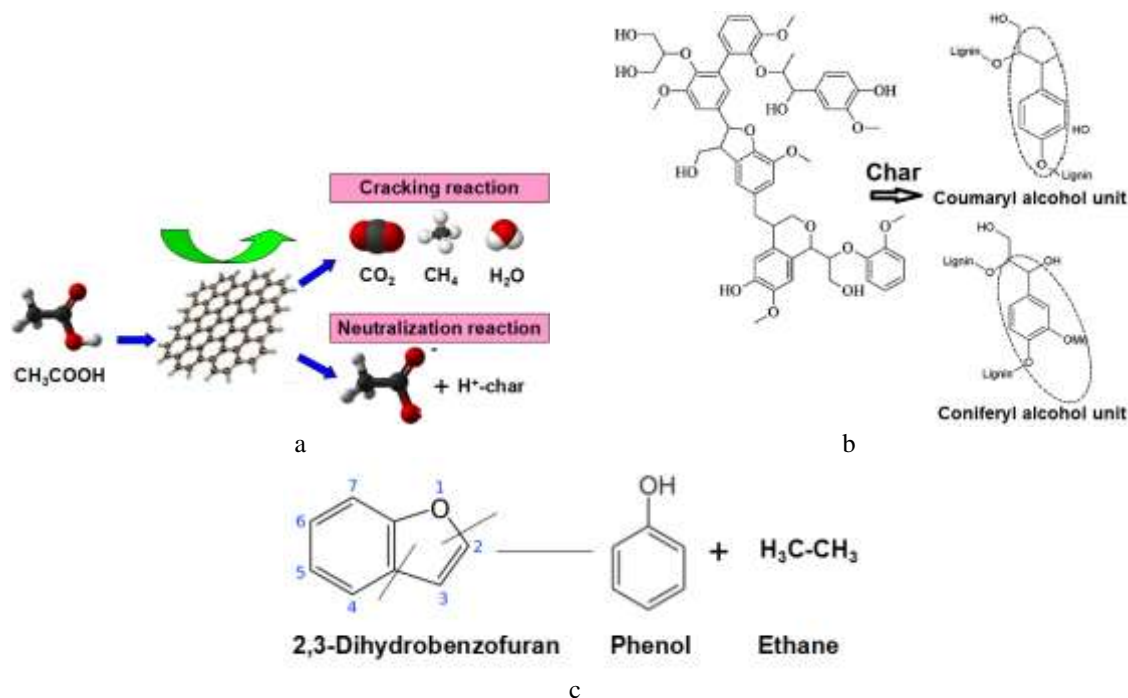
**Fig. 5.** Characteristics of the chars (a: FTIR of pore structure and Boehm titration results; b: ash composition)

### Catalytic Mechanism of Chars

As is known, acetic acid is mainly derived from the deacetylation of hemicellulose, furans are mainly from the degradation of cellulose, and phenols are from the degradation of lignin (Melligan *et al.* 2012). In this study, due to the effect of the char<sub>is</sub>, the acids in the bio-oil decreased and the phenolic substances increased. The acetic acid decomposition path is shown in Eqs. 1 through 3. Because the basicity of char<sub>is</sub> decreased after catalysis according to the Boehm titration result, the decrease of acetic acid might also have been attributed to the neutralization reaction in Eq. 4. Figure 6a shows the possible ways for acetic acid reduction that occurred in the pore channel of the char<sub>is</sub>.



In the char<sub>is</sub> catalytic process, the lignin may be catalytically converted into monomeric phenols through the following path shown in Fig. 6b (Melligan *et al.* 2012). The mesoporous structure of the char<sub>is</sub> provided a channel for the reaction. Iliopoulou *et al.* (2007) believed that the surface area and porous structure are important for enhancing the formation of phenols. As the previous results showed, after the char<sub>is</sub> catalysis the content of 2,3-dihydrobenzofuran was remarkably reduced. Thus, a second possible reaction path for phenols production is proposed as shown in Fig. 6c. Directional chemical bond cut occurred, and the 1-2 and the 3-4 bonds were broken, which resulted in phenol and ethane production. With an increased dose of char<sub>is</sub>, the volatile organics were further catalytically converted into phenol products, and the acetic acid was evidently reduced.



**Fig. 6.** Possible mechanism of catalytic reaction under char<sub>is</sub>: (a) acids inhibition; (b) lignin to phenols in char's action; (c) phenol promotion

## CONCLUSIONS

1. The present study demonstrated that it was feasible to use char as the catalyst for *in-situ* upgradation of biomass pyrolysis vapors. The quality of bio-oil was improved as the phenols were increased, and the acids were decreased in comparison to when there was no char<sub>is</sub> present.
2. The highest relative content of phenols was 55.6% (peak area percentage), obtained with a char<sub>is</sub> dose of 1.0 g (the char<sub>is</sub> to feed ratio was 0.25) at 550 °C, while the acetic acid was reduced from 31.4% to 17.2% (peak area percentage).
3. The product selectivity was not dependent upon the polar functional groups on the surface of char<sub>is</sub> according to the FTIR results, but it might have been dependent on the pore structures (mainly mesoporous) and the basicity sites of the char<sub>is</sub>, as well as the metallic species in the char<sub>is</sub>.
4. Three possible reaction mechanisms for catalytic process were proposed. Further experiments will be done to collect the evidence for the catalytic mechanism in detail.

## ACKNOWLEDGMENTS

The authors express their great gratitude for the financial support from Huadian Electric Power Research Institute Co., Ltd., the National Natural Science Foundation of China (51506071, 51622604), and the Fundamental Research Funds for the Central Universities.

## REFERENCES CITED

- Adam, J., Antonakou, E., Lappas, A., Stöcker, M., Nilsen, M. H., Bouzga, A., Hustad, J. E., and Øye, G. (2006). “*In situ* catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials,” *Micropor. Mesopor. Mat.* 96(1-3), 93-101. DOI: 10.1016/j.micromeso.2006.06.021
- Bartocci, P., Zampilli, M., Bidini, G., and Fantozzi, F. (2018). “Hydrogen-rich gas production through steam gasification of charcoal pellet,” *Appl. Therm. Eng.* 132, 817-823. DOI: 10.1016/j.applthermaleng.2018.01.016
- Elkasabi, Y., Mullen, C. A., Jackson, M. A., and Boateng, A. A. (2015). “Characterization of fast-pyrolysis bio-oil distillation residues and their potential applications,” *J. Anal. Appl. Pyrol.* 114, 179-186. DOI: 10.1016/j.jaap.2015.05.018
- Iliopoulou, E. F., Antonakou, E. V., Karakoulia, S. A., Vasalos, I. A., Lappas, A. A., and Triantafyllidis, K. S. (2007). “Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts,” *Chem. Eng. J.* 134(1-3), 51-57. DOI: 10.1016/j.cej.2007.03.066
- Keown, D. M., Hayashi, J. I., and Li, C. Z. (2008). “Effects of volatile–char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass,” *Fuel* 87(7), 1187-1194. DOI: 10.1016/j.fuel.2007.05.056

- Li, P., Li, D., Yang, H., Wang, X., and Chen, H. (2016). "Effects of Fe-, Zr-, and Co-modified zeolites and pretreatments on catalytic upgrading of biomass fast pyrolysis vapors," *Energ. Fuel.* 30(4), 3004-3013. DOI: 10.1021/acs.energyfuels.5b02894
- Li, Y., Shao, J., Wang, X., Deng, Y., Yang, H., and Chen, H. (2014). "Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption," *Energ. Fuel.* 28(8), 5119-5127. DOI: 10.1021/ef500725c
- Li, Y., Shao, J., Wang, X., Yang, H., Chen, Y., Deng, Y., Zhang, S., and Chen, H. (2013). "Upgrading of bio-oil: Removal of the fermentation inhibitor (furfural) from the model compounds of bio-oil using pyrolytic char," *Energ. Fuel.* 27(10), 5975-5981. DOI: 10.1021/ef401375q
- Lødeng, R., Hannevold, L., Bergem, H., and Stöcker, M. (2013). "Catalytic hydrotreatment of bio-oils for high-quality fuel production," in: *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, K. Triantafyllidis, A. Lappas, and M. Stöcker (eds.), Elsevier B.V., Amsterdam, Netherlands, pp. 351-396. DOI: 10.1016/B978-0-444-56330-9.00011-5
- Lu, Q., Zhang, Y., Tang, Z., Li, W.-Z., and Zhu, X.-F. (2010a). "Catalytic upgrading of biomass fast pyrolysis vapors with titania and zirconia/titania based catalysts," *Fuel* 89(8), 2096-2103. DOI: 10.1016/j.fuel.2010.02.030
- Lu, Q., Zhang, Z.-F., Dong, C.-Q., and Zhu X.-F. (2010b). "Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: An analytical Py-GC/MS study," *Energies* 3(11), 1805-1820. DOI: 10.3390/en3111805
- Mante, O. D., and Agblevor, F. A. (2011). "Catalytic conversion of biomass to bio-synchrude oil," *Biomass Conversion and Biorefinery* 1, 203-215. DOI: 10.1007/s13399-011-0020-4
- Melligan, F., Hayes, M. H. B., Kwapinski, W., and Leahy, J. J. (2012). "Hydro-pyrolysis of biomass and online catalytic vapor upgrading with Ni-ZSM-5 and Ni-MCM-41," *Energ. Fuel.* 26(10), 6080-6090. DOI: 10.1021/ef301244h
- Mortensen, P. M., Grunwaldt, J.-D., Jensen, P. A., Knudsen, K. G., and Jensen, A. D. (2011). "A review of catalytic upgrading of bio-oil to engine fuels," *Appl. Catal. A-Gen.* 407(1-2), 1-19. DOI: 10.1016/j.apcata.2011.08.046
- Papari, S., Hawboldt, K., and Helleur, R. (2017). "Production and characterization of pyrolysis oil from sawmill residues in an auger reactor," *Ind. Eng. Chem. Res.* 56(8), 1920-1925. DOI: 10.1021/acs.iecr.6b04405
- Qi, Z., Jie, C., Wang, T., and Ying, X. (2007). "Review of biomass pyrolysis oil properties and upgrading research," *Energ. Convers. Manage.* 48(1), 87-92. DOI: 10.1016/j.enconman.2006.05.010
- Ren, S., Ye, X. P., and Borole, A. P. (2017). "Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction," *J. Anal. Appl. Pyrol.* 123, 30-39. DOI: 10.1016/j.jaap.2017.01.004
- Sharma, R. K., and Bakhshi, N. N. (1993). "Catalytic upgrading of pyrolysis oil," *Energ. Fuel.* 7(2), 306-314. DOI: 10.1021/ef00038a022
- Stefanidis, S. D., Kalogiannis, K. G., Iliopoulou, E. F., Lappas, A. A., and Pilavachi, P. A. (2011). "In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor," *Bioresource Technol.* 102(17), 8261-8267. DOI: 10.1016/j.biortech.2011.06.032

Sun, Q., Yu, S., Wang, F., and Wang, J. (2011). "Decomposition and gasification of pyrolysis volatiles from pine wood through a bed of hot char," *Fuel* 90(3), 1041-1048. DOI: 10.1016/j.fuel.2010.12.015

Article submitted: February 13, 2018; Peer review completed: April 8, 2018; Revised version received: April 27, 2018; Accepted: April 28, 2018; Published: May 10, 2018. DOI: 10.15376/biores.13.3.4884-4896