

Hydrothermal Liquefaction of Desert Shrub *Salix psammophila* to High Value-added Chemicals and Hydrochar with Recycled Processing Water

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Bio-oil and hydrochar were produced through the hydrothermal liquefaction (HTL) of *Salix psammophila* (SP) branch residues with recycled processing water, in order to address the lack of water in deserts or sandy lands and the difficulty of water treatment in a batch reactor. The results indicated that the recycling of the HTL processing water could significantly improve the yield of bio-oil from 30.3% to 46.9%. The gas chromatography and mass spectrometry analyses of the obtained bio-oil confirmed the presence of value-added chemicals, such as phenolics, acetic acid, and furans. The acetic acid in the processing water played a key role in the HTL. The heavy oil had a high content (maximum of 42.7 wt%) of the low boiling point fraction (<300 °C), indicating its potential for further applications. The higher heating value of the hydrochar was about 27 MJ/kg, equivalent to the heating value of medium-rank and high-rank coals. These results show that HTL using recycled processing water has great potential for utilization of desert biomass wastes.

Keywords: *Salix psammophila*; Hydrothermal liquefaction; Recycled processing water; Bio-based chemicals; Hydrochar

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INTRODUCTION

The imbalance between the rapid consumption of fossil fuels and their slow formation has resulted in a serious global energy crisis. An effective route for diminishing this imbalance could involve the rapid conversion of organic waste and biomass into fuels and/or chemicals (Jin and Enomoto 2009). Hydrothermal liquefaction (HTL) is a promising second-generation method for the production of energy from biomass waste.

The HTL process converts wet biomasses into crude bio-oil at elevated temperatures (240 °C to 370 °C) and pressures (6 MPa to 25 MPa) and often involves homogeneous and/or heterogeneous catalysts to improve both the quality of the product and production yield (Toor *et al.* 2011). Under these conditions, water is in a subcritical phase characterized by the low viscosity and high solubility of the hydrophobic compounds, and it acts as both reactant and catalyst. Moreover, since wet feedstock can be directly used without drying (Demirbas 2010), the HTL of biomass to obtain bio-based chemicals and hydrochar has been studied extensively (Akahn *et al.* 2012; Kang *et al.* 2012; Yao *et al.* 2012). There have been many studies dealing with the hydrothermal conversion of biomass in the presence of different aqueous phases and chemical products (Jin and Enomoto 2009; Galletti *et al.* 2012). Jin and Enomoto (2009) researched the

hydrothermal conversion of different biomasses with use of a hydrogen peroxide (H₂O₂) aqueous solution to obtain low molecular weight carboxylic acids. Kang and colleagues characterized the hydrochar produced by the hydrothermal carbonization of lignin, cellulose, d-xylose, and wood meal (Kang *et al.* 2012). They showed that such hydrochar has significant potential for further applications as a solid fuel and adsorbents.

A great deal of processing water is produced from the HTL of biomass. This water contains a large number of phenolics, as shown in previous studies (Zhang *et al.* 2012; Pham *et al.* 2013). Thus, it is a source of environmental pollution and is difficult to dispose of (Yu *et al.* 2002; Arana *et al.* 2001). Most of the research has been focused on how to render it safe, rather than on its utilization as a resource. Kang recently researched the HTL of black liquor alkaline lignin and magnesium lignosulfonate at 320 °C (Kang *et al.* 2011). Their results indicated that the HTL products have the potential to become used as liquid antioxidants. The uses of black liquor and paper regeneration wastewater as a solvent in the HTL of plantation biomass have been researched (Sugano *et al.* 2008). Decreased residue yield and increased oil yield were observed with HTL when using the wastewater, in comparison to HTL using fresh water. The main compounds in processing water were glucose oligomers (Yu and Wu 2009), alcohols, phenol, and organic acids (Zhang *et al.* 2012; Pham *et al.* 2013).

On the other hand, the direct HTL of biomass in subcritical/supercritical solvents (*e.g.*, water, alcohols, and phenols) has been proven to be an efficient approach to convert biomass into low molecular weight chemicals (Wang *et al.* 2009). Therefore, if the processing water from an HTL procedure could be recycled for another HTL round without further treatment, the treatment process could be simplified and its cost could be reduced.

Salix psammophila (SP) is one of the dominant desert shrubs in northern China. It is planted to prevent wind erosion and control desertification and has played a significant role in local vegetation rehabilitation (Zhang and Huang 2006). However, this kind of shrub has a special biological characteristic: Their stems should be cut once every 3 to 5 years in order for the plants to flourish. In order to maintain a benign ecological system, the systematic cutting and curing of the shrub is necessary, producing a large amount of SP branch residues. The main contents of SP are lignocellulose, including hemicellulose, cellulose, and lignin, which is great feedstock for the production of bio-based chemicals and hydrochar, such as carboxylic acids, phenolic derivatives, furan compounds, solid fuel, and adsorbents.

The main objective of the present work is the verification of the potential of the HTL technique for conversion of SP branch residues to high value-added compounds, depending on the effects of temperature, reaction time, liquor ratio, and recycling rounds of the processing water. Liquefaction products (bio-oils and hydrochar) were examined by using gas chromatography and mass spectrometry (GC-MS), thermogravimetric analysis (TGA), and elemental analysis (EA).

EXPERIMENTAL

Materials

SP branches obtained from the sandy land of Xilinguole in Inner Mongolia, northern China, were used as the raw material. They were oven-dried at 105 °C for 12 h and then milled into powder (40 to 100 mesh) for HTL. As shown in Table 1, the raw

material had a low content of moisture (8.9%) and ash (1.60%) and a high content of volatile matter (79.78%). The volatile matter was determined by means of proximate analysis of coal (GB/T 212-2008, China. CN-GB, 2008). The cellulose, hemicellulose, and lignin contents were 55.45, 18.89, and 25.89%, respectively. The lignin content was lower than for hardwood, but higher than for other lignocellulose biomass.

Table 1. Proximate Analysis and Compositions of Raw Material

Proximate Analysis (%)	
Moisture	8.9
Ash	1.6
VM ^a	79.78
Compositions (% Dry Basis)	
Cellulose ^b	55.45
Hemicellulose ^b	18.89
Lignin ^c	25.49

^aVM, volatile matter. ^bThe composition was analyzed by GB/T2677.10-1995(GB/T2677-1995, China. CN-GB, 1995). ^cThe composition was analyzed by GBT10337-2008(GB/T10337-2008, China. CN-GB, 2008).

Hydrothermal Conversion and Product Separation

The experiments were performed using an HTL system—a 250-mL GSH-0.25 zirconic alloy cylindrical autoclave heated by an external electrical furnace and equipped with a magnetic stirrer. The system was similar to previous studies (Zhou *et al.* 2010; Zhang *et al.* 2012).

In a typical experimental run, 30 g of SP powder and 150 mL of distilled water were charged into an autoclave, which was then sealed firmly. Residue air was purged with pure N₂ for 5 min. The autoclave was pressurized to 2 MPa, using pure N₂ to suppress cracking from the boiling of the water during the liquefaction process. When the temperature reached the set value, it was maintained for a certain time, which has been defined as the reaction time.

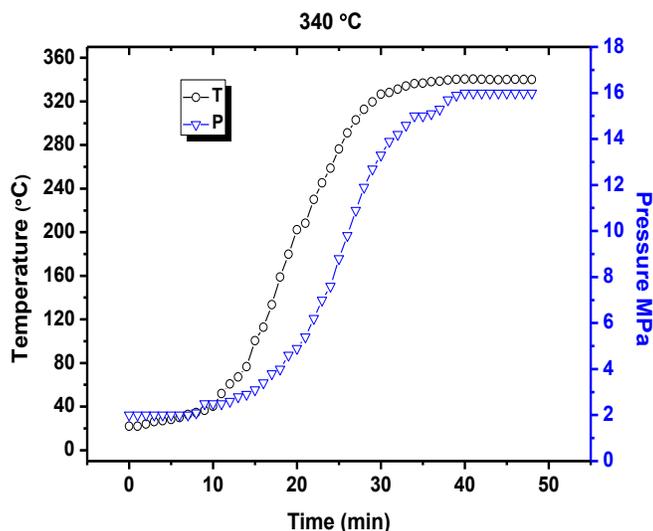


Fig. 1. Temperature and pressure variations during HTL

The autoclave was cooled to room temperature with running water. The gaseous product was vented, and the autoclave was opened. The total reaction product in the autoclave was fully collected. During the HTL procedure, the pressure inside the autoclave varied with temperature, depending on the solution vapor pressure and gas fraction (Fig. 1).

The separation procedure of the reaction product is illustrated in Fig. 2. The collected reaction product was first filtered with a Buchner funnel; the processing water was extracted with ether using a separatory funnel; and the remaining processing water was considered to be ether-insoluble (EI). The ether-soluble fraction was evaporated at 35 °C under reduced pressure in a rotary evaporator to completely remove the ether, and the residue is designated as water-soluble oil (WSO).

About 150 mL of tetrahydrofuran (THF) was used to wash the solid phase, and the mixture was filtered with a Buchner funnel. The THF-soluble fraction was then evaporated at 65 °C under reduced pressure in a rotary evaporator to completely remove the THF, and the residue is described as heavy oil (HO). HO and WSO together were defined as total oil (TO). The THF-insoluble residues were dried at 105 °C for 12 h and are defined as hydrochar (HC).

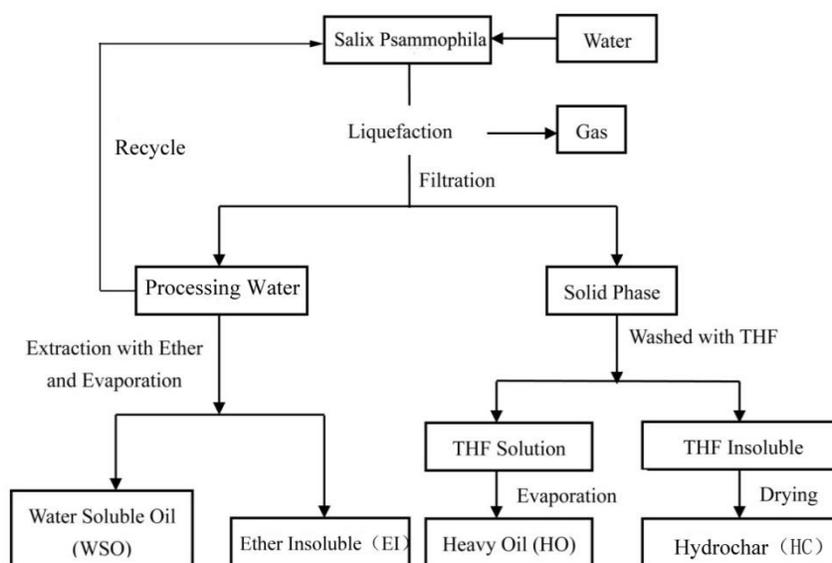


Fig. 2. Product separation procedure

The HTL products included HO, WSO, HC, and EI. The yields of all these products were calculated with the following equations:

$$\text{Yield of HO} = \frac{\text{mass of HO}}{\text{mass of feed}} \times 100\% \quad (1)$$

$$\text{Yield of WSO} = \frac{\text{mass of WSO}}{\text{mass of feed}} \times 100\% \quad (2)$$

$$\text{Yield of HC} = \frac{\text{mass of HC}}{\text{mass of feed}} \times 100\% \quad (3)$$

$$\text{Yield of EI} = \frac{\text{mass of EI}}{\text{mass of feed}} \times 100\% \quad (4)$$

$$\text{Yield of TO} = \text{Yield of HO} + \text{Yield of WSO} \quad (5)$$

$$\text{HHV improvement (\%)} = \frac{\text{HHV of HC} - \text{HHV of raw material}}{\text{HHV of raw material}} \times 100\% \quad (6)$$

When the processing water was recycled, the mass of the feed (N) was equal to the mass of the raw material plus the mass of WSO (N-1) plus the mass of EI (N-1), where N is the number of recycling rounds of the processing water.

Product Analysis

GC-MS

GC-MS analysis of HO was performed on a Thermo FOCUS DSQ with an HP-5 ms column (5% phenyl and 95% dimethylpolysiloxane, 30mm × 0.25 mm × 0.25 μm). The carrier gas was helium with a flow rate at 1 mL min⁻¹. A total of 1 μL of THF solution of HO (0.15 g 10 mL⁻¹ THF) was injected into the column. The GC oven temperature program was as follows: hold at 60 °C for 2 min, raise to 300 °C with a heating rate of 20 °C min⁻¹, and hold for 5 min.

GC-MS analysis of WSO was carried out using a Finnigan Voyager with a HP-INNOWax column (100% polyethylene glycol, 30 mm × 0.25 mm × 0.25 μm). The carrier gas was also helium with a flow rate of 1 mL min⁻¹. A total of 1 μL ether solution of WSO (0.10 g 10 mL⁻¹ ether) was injected into the column. The GC oven temperature program was as follows: hold at 60 °C for 2 min, raise to 250 °C with a heating rate of 15 °C min⁻¹, and hold for 10 min.

Identification of compounds was performed by analyzing the MS data using the HP ChemStation software. The matching degrees of all the identified compounds with known MS spectra were above 80%. And it should be noted that only a fraction of the oil products obtained in this research can be identified by GC-MS due to the temperature limit of the instrument (maximum boiling point detected ~ 300 °C).

EA

The elemental compositions of raw materials and hydrochars were analyzed with an Elemental Analyzer Vario EL III instrument.

TGA

The TGA of raw material and HO were analyzed by thermo-gravimetric analyzer 7 (Perkin Elmer, USA) from room temperature to 900 °C.

RESULTS AND DISCUSSION

Effects of Reaction Temperature on Product Yields

The reaction temperature of HTL is a critical factor affecting the product yields. Reaction temperatures in the range of 240 °C to 340 °C were investigated according to previous studies (Zhou *et al.* 2010; Kang *et al.* 2011). Figure 3A exhibits a graphic expression of the product yield variations with temperature. As can be seen from the

figure, the HO yield increased in the temperature range of 240 °C to 300 °C and then decreased at 320 °C. The same trends had been found in previous studies (Zhou *et al.* 2010; Sugano *et al.* 2008). Secondary decompositions and gas reactions become active at high temperatures, resulting in the formation of gases and the recombination of free radical reactions and leading to char formation due to their high concentrations (Akhtar and Amin 2011). The highest HO yield was obtained at 300 °C (25.73%) and the lowest at 240 °C (17.47%).

A rapid decrease in the HC yield from 38.00% to 16.14% was observed with increasing reaction temperature. The EI yield slightly increased from 240 °C to 280 °C and then decreased at 300 °C. The WSO yield varied very little, with a range of 4.17 to 5.07%. The TO yield variation was, therefore, almost the same as that of HO.

The lignin content is also a critical factor for HTL product yields. The best temperature for HTL of SP was 300 °C. The lignin content of SP is 25.89 wt%, which is lower than that of Chinese fir (32.44%) (Zhong and Wei 2004) and similar to that of Manchurian ash (21%) (Zhong and Wei 2004). The HTL of Chinese fir and Manchurian ash have been researched by Zhong and colleagues. Their results indicated that the best temperature for HTL of Chinese fir and Manchurian ash is 340 °C and 300 °C, respectively (Zhong and Wei 2004). The higher the lignin content, the greater the temperature required for HTL.

Effects of Liquor Ratio and Reaction Time on Product Yields

Figure 3B shows the effect of the reaction time on product yields at 300 °C with a liquor ratio (distilled water / raw material, mL g⁻¹) of 5. The HO yield increased with reaction time increasing from 0 minutes to 10 minutes, but it decreased at 30 minutes. The HC yield had the opposite trend. The EI yield decreased with increased reaction time, while the WSO yield increased. Secondary reactions take place during the HTL process, at which HO and EI can gasify or repolymerize into HC (Sato *et al.* 2003). Previous biomass HTL studies also showed that shorter residence times favored the bio-oil yields (Akahn *et al.* 2012; Wang *et al.* 2008).

Figure 3C shows the effect of the liquor ratio on product yields at 300 °C with a reaction time of 10 minutes. The HO yield decreased with liquor ratio increases from 5 to 10, while the HC and WSO yields increased. This result is different from previous studies (Sato *et al.* 2003; Wang *et al.* 2008). At low liquor ratios, the relative interactions among molecules of the biomass and water become less influential, which can suppress dissolution of the biomass components. A high liquor ratio is suitable for the production of liquid and gas, due to the enhanced extraction by a denser solvent medium. However, Bookcock and Sherman observed that the amount of liquid oils decreased significantly at very high liquor ratios (Bookcock and Sherman 2009).

Effects of the Recycling of the Processing Water on Product Yields

Due to the scarcity of water in deserts or sandy lands, the focus was on investigating the effect of recycling of the processing water on product yields. Figure 3D shows that the recycling of the processing water had a great effect on product yields. The TO, WSO, and EI yields increased as the rounds of processing water recycling increased from zero to three, while the HC yield decreased. The compounds in EI and WSO could improve the HTL of SP. The recycled processing water resulted in an HO with improved flowability.

Yin and Tan researched the HTL of cellulose to bio-oil under acidic, neutral, and

alkaline conditions (Yin and Tan 2012). Their results indicated that the bio-oil yield under acidic conditions was much higher than under neutral and alkaline conditions. The pH values of the processing water decreased as the recycling rounds increased. The initial pH value was 4.52, and the final pH values decreased to 3.41 when the processing water was recycled for the third time. The decrease of pH after HTL was mainly caused by the formation of carboxylic acids from the biomass, such as lactic acid, acetic acid, and formic acid (Hsieh *et al.* 2009). Table 4 indicates that the main compounds of the WSO were acetic acid and phenolics.

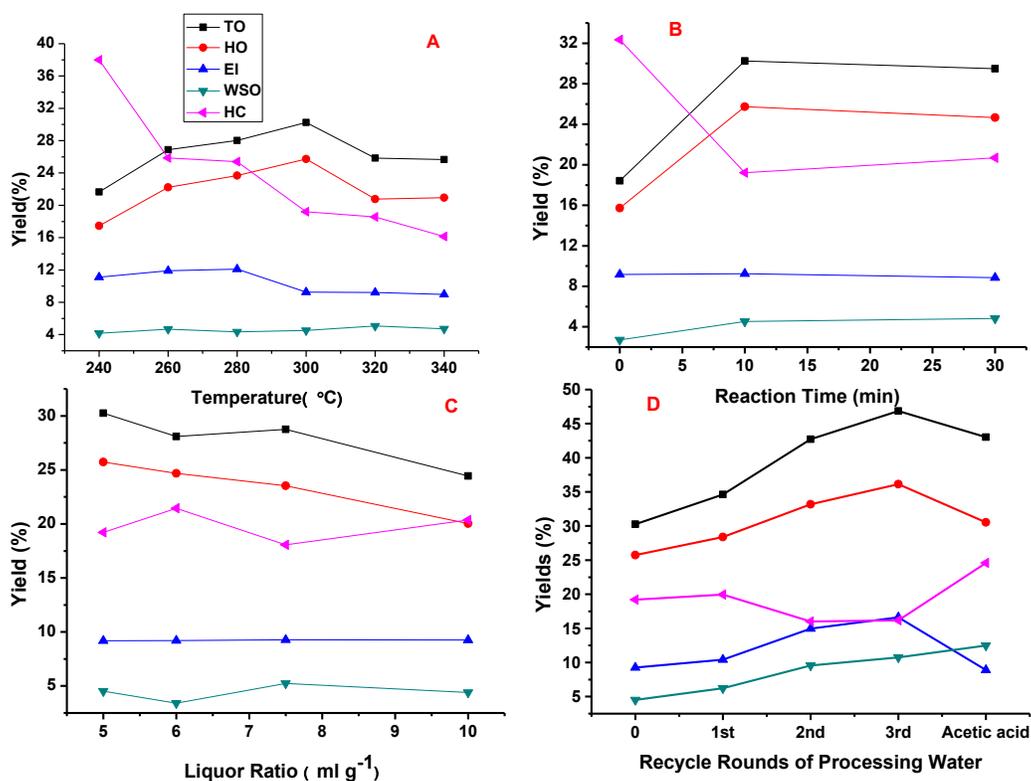


Fig. 3. Effects on product yields of (A) temperature, (B) liquor ratio, (C) reaction time, and (D) recycling rounds of processing water

Previous studies showed that organic acids and phenols as the liquefaction medium could promote the liquefaction of biomass (Yip *et al.* 2009; Ross *et al.* 2010). Ross and colleagues researched the HTL of microalgae (*Chlorella* and *Spirulina*) using acetic acid, and their results indicated that acetic acid could considerably improve the bio-crude yield (Ross *et al.* 2010).

In order to verify that the acetic acid in the processing water is the main factor affecting the bio-oil yield, acetic acid (AC) was added to the water (pH: 2.57) as a catalyst. The results showed that the HO yield with AC as catalyst was higher than that of the zero and first recycling rounds of the processing water, but lower than that of the second and third rounds. The main reason is that high concentration acetic acid could promote the hydrolysis of lignin to phenolic products, but it also could promote the condensation of the phenolic products to solid residue (Liu *et al.* 2006). So the HC yield was higher than that without the addition of acetic acid. The acetic acid of the processing water did, indeed, play a key role in the product yields.

Analysis of HO, WSO, and HC

GC-MS analysis of HO and WSO

As can be seen in Table 2, the compounds identified in HO could be classified into seven groups, including phenolics, furans, long-chain alkanes, cyclopentenones, alcohols, acids, and ketones. Phenolics (31.12% to 67.89%) and furans (0% to 16.23%) were the main compounds. Table 2 shows the peak areas of 2-methoxyphenol (retention time (RT) = 6.26 min), 4-ethyl-2-methoxyphenol (RT = 7.78 min), and 2,6-dimethoxyphenol (RT = 8.3 min) increased with increased reaction temperatures. Interestingly, the study of Wahyudiono and colleagues showed that higher temperatures were conducive to conversion of the methoxyl aromatic products (Wahyudiono *et al.* 2007).

The 5-(hydroxymethyl)-furfural (5-HMF, RT = 7.33 min) disappeared at 280 °C. The 5-HMF resulted from the hydrothermal conversion of cellulose under acidic and neutral conditions (Yin and Tan 2012); however, the 5-HMF was unstable at higher temperatures. The 5-methylfuran-2-carbaldehyde (MF, RT = 5.16 min) disappeared at 300 °C, and the tetrahydro-2-furanol (RT = 3.24 min) was observed only at 300 °C (15.79%). The total peak area of furans decreased steeply from 300 °C to 340 °C, and the total identified area of phenolics increased significantly, indicating that phenolics could be formed from the decomposition of furfural and furfural derivatives (Anastasakis and Ross 2011).

The GC-MS total ion chromatogram and analysis results of HO obtained with different recycling rounds of the processing water are shown in Table 3. It can be seen that the total peak area of phenolics increased significantly from 37.2% to 42.4% with increases in the number of recycling rounds of the processing water. However, the total identified area of phenolics slightly decreased, which is attributed to the buffering effect of acetic acid when recycling rounds increased.

The phenolics had a significant increase from 37.2% to 53.26% when acetic acid was used as the catalyst. This result is in good agreement with those of Ross and colleagues (Ross *et al.* 2010). They researched bio-crude obtained from the HTL of microalgae (*Chlorella* and *Spirulina*) using acetic acid, and their results indicated that larger amounts of phenolics appeared in the bio-crude after using organic acids. Therefore, acetic acid in the processing water is the main factor that leads to higher phenolics. The high content of phenolics may be attributed to the decomposition of lignin and the secondary polymerization of products formed from the decomposition of cellulose (Kruse *et al.* 2007; Anastasakis and Ross 2011). Acetic acid can also assist in the decomposition of lignin.

Table 4 lists the GC-MS analysis results of WSO with different recycling rounds of the processing water. The chromatogram suggests that the WSO mixtures mainly consisted of small molecular compounds, including ketones, carboxylic acids, phenolics, and furans. The main WSO components were acetic acid (17.7% to 29.5%) and phenolics. Most of the acetic acid was from the hydrolysis of cellulose (Qu *et al.* 2003). It was formed by the decomposition of both furfurals and phenols. The ketones and furans (RT of 7–9 min) increased with acetic acid used as a catalyst.

Although the compounds of the WSO and HO products obtained were highly complex, it should be noted that the contents of the acetic acid and phenolics were much higher than the contents of other compounds, which makes it possible to separate out bio-based chemicals from bio-oil.

Table 2. GC-MS Analysis Results of HO Obtained at Different Temperatures

Compound Name	RT ^a	Temperature (°C) / Area (%)					
		240	260	280	300	320	340
Lactones and Acid		- ^b	-	-	7.84	-	-
Butyrolactone	4.61	-	-	-	3.25	-	-
n-Hexadecanoic acid	11.8	-	-	-	4.59	-	-
Ketone and Alcohol		4.98	5.06	4.33	1.67	4.59	-
2,5-Hexanedione	4.72	-	-	-	0.38	-	-
Benzyl alcohol	5.76	4.98	5.06	4.33	1.29	4.59	-
Cyclopentenone		2.28	2.74	2.28	4.14	0.18	7.49
2-Cyclopenten-1-one.	3.78	-	-	-	0.32	-	-
2-Cyclopenten-1-one.2-methyl-	4.53	-	-	-	1.32	-	-
2-Cyclopenten-1-one.3-methyl-	5.14	-	-	-	0.6	0.18	0.90
2-Cyclopenten-1-one.2,3-dimethyl-	5.43	-	-	-	0.52	-	5.65
2-Cyclopenten-1-one.2-hydroxy-3-methyl-	5.70	2.28	2.74	2.28	1.09	-	-
2-Cyclopenten-1-one.3-ethyl-	6.18	-	-	-	0.29	-	-
2-Cyclopenten-1-one.2,3,4-trimethyl-	6.29	-	-	-	-	-	0.94
Phenolics		31.1	44.0	49.2	37.2	55.7	67.9
Phenol	5.19	6.38	7.02	5.96	2.47	3.46	3.17
Phenol.2-methoxy-	6.26	6.4	9.65	12.5	9.09	14.4	17.2
Phenol.2-methyl-	5.89	-	-	-	0.63	-	-
Phenol.3-methyl-	6.07	-	-	-	1.22	1.09	0.95
Phenol.4-methyl-	6.04	-	1.35	2.17	-	2.01	2.69
Phenol.4-ethyl-	6.83	-	-	-	-	1.04	-
1,2-Benzenediol	7.07	-	-	-	2.03	-	-
Phenol.2-methoxy-4-methyl-	7.12	-	-	-	1.92	4.56	6.92
1,2-Benzenediol.3-methoxy-	7.67	-	-	-	1.05	-	3.09
Phenol.4-ethyl-2-methoxy-	7.78	2.02	3.32	4.87	5	6.15	7.18
2'6'-Dihydroxyacetophenone	7.80	-	1.2	1.09	-	0.72	-
Benzaldehyde.4-hydroxy-	8.03	-	0.81	-	-	-	-
1,4-Benzenediol.2-methyl-	8.19	-	-	-	0.63	-	-
Phenol.2,6-dimethoxy-	8.30	7.40	10.3	15.5	11.2	18	19.8
Phenol.2-methoxy-4-propyl-	8.42	-	-	-	1.26	1.24	1.74
Vanillin	8.70	2.79	2.48	3.07	-	1.15	-
5-tert-Butylpyrogallol	9.89	-	-	-	-	-	5.16
Benzaldehyde.4-hydroxy-3,5-dimethoxy-	10.4	4.23	3.35	2.48	-	0.78	-
Phenol.2,6-dimethoxy-4-(2-propenyl)-	10.6	1.9	1.4	-	-	-	-
Ethanone.1-(4-hydroxy-3,5-	10.8	-	1.15	1.53	0.68	1.05	-
Phenol.2-methoxy-4-(1-propenyl)-	11.1	-	1.94	-	-	-	-
Furan		13.6	8.94	1.76	16.2	-	0.93
2-Furancarboxaldehyde.5-methyl-	5.16	7.51	3.32	1.76	-	-	-
Benzofuran.2-methyl-	6.46	-	-	-	0.44	-	-
2-Furanol.Tetrahydro-	6.50	-	-	-	15.8	-	-
2-Furanmethanol.Tetrahydro-.acetate	7.19	-	-	-	-	-	0.93
2-Furancarboxaldehyde.5-(hydroxymethyl)-	7.33	6.09	5.62	-	-	-	-
Long-chain alkane		9.38	5.04	3.11	-	2.49	-
Elcosane	14.3	9.38	5.04	3.11	-	2.49	-
Others		-	-	-	1.55	1.78	0.76

^a RT retention time (minutes). ^b - undetectable

Table 3. GC-MS Analysis Results of HO with Different Recycling Rounds of the Processing Water

Compound Name	RT ^a	Area (%)				
		0	1 st	2 nd	3 rd	AC ^b
Butyrolactone	4.61	3.25	2.76	2.04	1.65	- ^c
2,5-Hexanedione	4.72	0.38	0.92	0.94	0.80	-
3,6-Heptanedione	5.64	-	-	-	0.44	-
Benzyl alcohol	5.76	1.29	1.49	1.68	1.49	-
Cyclopentenone		4.14	3.74	5.25	5.09	1.25
2-Cyclopenten-1-one.	3.78	0.32	0.32	0.64	0.46	-
2-Cyclopenten-1-one.2-methyl-	4.53	1.32	1.4	1.96	1.89	1.25
2-Cyclopenten-1-one.3-methyl-	5.14	0.60	0.65	0.90	0.85	-
2-Cyclopenten-1-one.3,4-dimethyl-	5.38	-	-	0.29	0.31	-
2-Cyclopenten-1-one.2,3-dimethyl-	5.43	0.52	0.93	0.69	0.88	-
2-Cyclopenten-1-one.2-hydroxy-3-methyl-	5.70	1.09	0.44	0.42	0.27	-
2-Cyclopenten-1-one.3-ethyl-	6.18	0.29	-	0.35	0.43	-
Phenolics		37.2	42.4	39.8	38.2	53.26
Phenol	5.19	2.47	3.43	3.46	2.97	-
Phenol.2-methyl-	5.89	0.63	0.66	1.14	0.27	-
Phenol.3-methyl-	6.07	1.22	1.17	1.28	1.20	-
Phenol.2-methoxy-	6.26	9.09	9.14	9.98	9.97	22.54
1,2-Benzenediol	7.07	2.03	3.01	2.75	2.00	-
Phenol.2-methoxy-4-methyl-	7.12	1.92	1.42	1.21	1.30	3.84
1,2-Benzenediol.3-methyl-	7.59	-	-	-	0.20	-
1,2-Benzenediol.3-methoxy-	7.67	1.05	0.99	0.91	1.34	-
Phenol.4-ethyl-2-methoxy-	7.78	5.00	5.02	4.04	3.80	10.2
1,4-Benzenediol.2-methyl-	8.19	0.63	0.95	0.63	0.52	-
Phenol.2,6-dimethoxy-	8.30	11.2	15.6	13.8	13.6	16.72
Phenol.2-methoxy-4-propyl-	8.42	1.26	0.97	0.65	0.95	-
Ethanone.1-(4-hydroxy-3,5-dimethoxyphenyl)	10.75	0.68	-	-	-	-
Furan		16.2	21.6	19.4	18.0	3.49
2-Furanol.Tetrahydro-	3.24	15.8	20.2	19.1	17.2	3.49
Ethanone.1-(2-furanyl)-	4.52	-	0.27	-	0.50	-
Benzofuran.2-methyl-	6.46	0.44	0.42	0.31	0.27	-
2-Methyl-5-hydroxybenzofuran	8.77	-	0.74	-	-	-
n-Hexadecanoic acid	11.8	4.59	-	3.06	2.80	4.95
Tetratetracontane	14.5	-	-	2.11	-	4.58
Elcosane.10-methyl-	14.7	-	-	-	-	1.72
1-Heneicosylformate	15.8	-	-	-	-	1.63
Others	9.27-9.54	1.55	2.30	1.62	1.72	-

^a retention time. ^b acetic acid. ^c undetectable.

Table 4. GC-MS Analysis of the WSO Main Compounds with Different Recycling Rounds of the Processing Water

No.	RT ^a	Compound Name	MW ^b	Area (%)				
				0	1 st	2 nd	3 rd	AC ^c
1	2.90	Ethyl acetone	86	0.30	0.30	0.68	0.64	- ^d
2	3.61	3-Hexanone	100	0.04	0.10	0.18	0.05	-
5	4.73	3-Buten-1-ol	72	0.07	0.06	0.11	0.11	-
6	4.96	Cyclopentanone	84	1.35	1.03	0.54	1.34	0.50
7	5.22	Cyclopentanone,3-methyl-	98	0.41	0.23	0.09	0.34	0.15
8	5.46	3-Hydroxy-3-methyl-2-butanone	102	0.18	0.18	0.23	0.20	0.05
9	5.93	Cyclohexanone	98	1.21	0.74	0.82	0.64	0.15
10	6.48	2-Cyclopenten-1-one	82	2.25	2.20	2.47	1.98	1.08
11	6.54	2-Cyclopenten-1-one,2-methyl-	96	4.06	3.88	4.53	3.95	2.59
12	6.97	Acetic acid	60	17.7	24.6	29.5	26.3	53.8
13	7.22	Furfural	96	0.76	0.53	0.52	0.45	-
14	7.60	2-Cyclopenten-1-one,3,4-dimethyl-	110	-	-	-	-	0.49
15	7.72	Propanoic	74	3.52	2.57	1.77	4.48	-
16	7.72	2,5-Hexanedione	114	-	-	-	-	2.35
17	7.90	2-Cyclopenten-1-one,3-methyl-	96	-	-	-	-	0.75
18	8.02	2-Cyclopenten-1-one,2,3-dimethyl-	110	-	-	-	-	1.05
19	8.46	2-Acetyl-5-methylfuran	124	-	-	-	-	0.27
20	8.51	2(3H)-Furanone,dihydro-5-methyl-	100	-	-	-	-	0.12
21	9.53	2-Cyclopenten-1-one,2-hydroxy-3-methyl-	112	1.41	0.62	0.48	1.23	-
22	9.70	Phenol,2-methoxy-	124	6.23	5.92	2.77	5.79	-
23	9.77	Benzyl alcohol	108	3.24	3.28	0.42	2.56	2.67
24	9.88	Phenol,2-methoxy-	124	-	-	-	-	5.38
25	9.90	2-Cyclopenten-1-one,3-ethyl-2-hydroxy-	126	0.34	0.49	0.36	0.37	1.56
26	9.99	Phenyl-ethyl alcohol	122	0.28	0.22	0.71	0.28	-
27	10.2	2-Methoxy-5-methylphenol	138	1.49	0.87	0.45	0.78	-
28	10.5	Phenol	94	3.38	3.24	3.11	3.02	3.24
29	10.6	Phenol,4-ethyl-2-methoxy-	152	1.37	1.02	0.76	0.87	0.76
30	10.9	Phenol,4-methyl-	108	0.55	0.41	0.36	0.34	0.15
31	10.9	Phenol,3-methyl-	108	0.55	0.45	0.12	0.39	0.24
32	11.3	Phenol,4-ethyl-	122	0.27	0.20	0.16	0.14	-
33	11.6	Phenol,3,4-dimethyl-	122	0.15	0.14	0.09	0.13	-
34	11.8	Phenol,2,6-dimethoxy-	154	7.85	9.99	7.34	9.07	9.32
35	13.8	Vanillin	152	0.97	0.88	0.59	0.62	1.05
36	14.3	Ethanone,1-(4-hydroxy-3-methoxyphenyl)-	166	0.46	0.55	0.78	0.38	0.39
37	17.1	Ethanone,1-(3-hydroxyphenyl)-	136	0.38	0.52	0.30	0.43	-
38	18.9	3,5-Dihydroxytoluene	124	2.28	3.20	1.15	2.45	-
39	19.7	Hydroquinone	110	1.11	1.62	0.94	1.50	-

^a retention time (minutes). ^b molecular weight. ^c acetic acid. ^d undetectable.

TGA of HO

The boiling point distribution of the HO obtained at different reaction temperatures and recycling rounds of the processing water was assessed by using thermal gravimetric analysis (TGA) in nitrogen, as described by Ross *et al.* (2010). The boiling point distribution at intervals of 50 °C is listed in Table 5 for the main experiments performed. Heating the HO under an inert atmosphere to 900 °C typically resulted in a mass loss of 70 to 80 wt%. Table 5 indicates that all of the HO products contained significant amounts of high boiling point compounds. Compounds that had a boiling point of more 300 °C were amenable to GC-MS (oven temperature of 300 °C). Increases in temperature resulted in a significant increase in the percent of the total weight from 30.39% (240 °C) to 42.73% (300 °C). The low molecular compounds may have repolymerized into high molecular compounds with the increases in temperature. Therefore, the percent of the total weight (<300 °C) had the same variation trend as the HO yield with the effect of temperature. These results were very similar to those of Anastasakis and Ross's study (2011). Their results showed that the percent of the total weight (<300 °C) of the bio-crude from HTL of brown macro-alga *Laminaria saccharina* was between 33% and 42%.

Table 5 indicates that the percent of the total weight (<300 °C) of HO had only a slight difference with the recycling of the processing water and the use of acetic acid as a catalyst, which is similar to a study by Yip and colleagues (2009). They researched the liquefaction process and liquefied products from bamboo using different organic solvents, and their results showed the low boiling point products of liquefied bamboo were similar, regardless of the type of solvent used. This result agrees with the GC-MS data shown in Table 3, which indicates that the identified compounds and area of HO had only subtle differences.

Table 5. Boiling Point Distribution of HO Obtained at Different Temperatures and Recycling Rounds of the Processing Water

Boiling Point of HO (°C)	Percent of the Total Weight (wt%)										
	Temperature						Recycling Rounds of Processing Water				
	240°C	260°C	280°C	300°C	320°C	340°C	0	1 st	2 nd	3 rd	AC ^a
20–300	30.4	36.4	31.0	42.7	36.4	32.4	42.7	33.9	37.1	41.0	37.5
300–350	9.12	10.2	11.0	11.9	4.24	5.20	11.9	5.93	8.85	10.9	7.87
350–400	6.81	6.00	8.09	9.70	8.32	10.4	9.70	12.6	10.1	10.3	7.30
400–450	5.77	4.69	4.36	3.99	7.89	7.22	3.99	8.60	5.97	4.31	6.02
450–500	4.30	3.61	3.41	2.54	3.26	3.16	2.54	3.33	2.78	2.34	3.60
500–550	3.10	1.93	2.07	1.55	3.84	2.28	1.55	2.45	1.90	1.47	1.66
550–900	22.1	6.70	5.06	4.47	30.7	13.2	4.47	19.1	6.80	3.70	11.3

^a acetic acid.

Chemical Properties of HC and HO

As shown in Table 6, the carbon content, the ratios of carbon/oxygen and carbon/hydrogen, and the improvement in the higher heating values (HHVs) in all of these HC were 57.8 to 70.4%, 1.59 to 3.07, 11.4 to 13.2, and 26.8 to 66.7%, respectively. The higher heating value (HHVs) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced (Makecat-bot 2013). The HHVs were calculated by use of the Dulong formula (Xu and Lad 2007): HHV (MJ/kg) = 0.3383 C + 1.422 (H - O/8). The basic

trends were that these values increased as the temperature increased. The improvement in the carbon content was mainly due to deoxygenating reactions, and it has been reported that both dehydration and decarboxylation occur during hydrothermal carbonization (Berge *et al.* 2011; Sevilla *et al.* 2011). The higher heating values (HHVs) of these HC were 21 to 27 MJ/kg, which is equivalent to the heating value of medium-rank and high-rank coals, according to the Chinese National Standard (GB/T 15224.3-2010, China.CN-GB, 2010).

The carbon recoveries of HC and HO obtained at different temperatures and recycling rounds of the processing water are shown in Fig. 4A and 4B, respectively. The carbon recovery rate of HC decreased with increased reaction temperatures and increased number of recycling rounds of the processing water. From Fig. 5B, it can be seen that the carbon recovery of HO had the same variation trend as the HO yield as a result of increased temperature and increased number of recycling rounds of the processing water. The highest HO carbon recovery rate was 49.97%, which indicates that the recycling of processing water is an effective method to obtain bio-oil products through HTL.

The total carbon recovery (HO and HC) increased in the temperature range of 240 °C to 280 °C, and then decreased at 300 °C, indicating that at higher temperatures the volatile matter was converted to other products, probably carbon dioxide (CO₂) and other gases. The total carbon recovery was in the range of 52% to 80%, with the other remaining carbon recovery from the EI, WSO, and gas. The HC carbon recovery with acetic acid was higher than that without the addition of acetic acid, which is very consistent with acetic acid promotion of the introduction of HC.

Table 6. Proximate Analysis, HHV Calculation of Raw Materials, and HC (Wt%)^a

	C (%)	H (%)	N (%)	O ^b (%)	C/H	C/O	HHV (MJ/Kg)	HHV Improvement (%)
Raw material	48.3	5.60	0.73	43.8	8.61	1.10	16.5	
Temperature (°C)								
240	57.8	5.50	0.49	36.2	10.5	1.59	20.9	26.8
260	64.4	5.65	0.84	29.1	11.4	2.21	24.7	49.5
280	68.7	5.35	0.57	25.4	12.8	2.70	26.4	59.5
300	69.1	5.58	1.29	24.0	12.4	2.87	27.1	64.0
320	70.4	5.34	1.06	23.2	13.2	3.04	27.4	65.6
340	69.5	5.63	2.24	22.7	12.3	3.07	27.5	66.7
Recycling rounds of processing water								
0	69.1	5.58	1.29	24.0	12.4	2.87	27.1	64.0
1 st	68.4	5.89	1.13	24.6	11.6	2.79	27.2	64.7
2 nd	66.3	5.49	1.36	26.9	12.1	2.47	25.5	54.4
3 rd	67.7	5.00	0.80	26.5	13.6	2.56	25.4	53.5
AC ^c	67.3	5.83	0.64	26.2	11.5	2.57	26.5	60.2

^a All measured on a dry basis. ^b By mass difference. ^c acetic acid.

The chemical properties and functional groups results are significant for further application (e.g., solid fuel, adsorption) studies of HC.

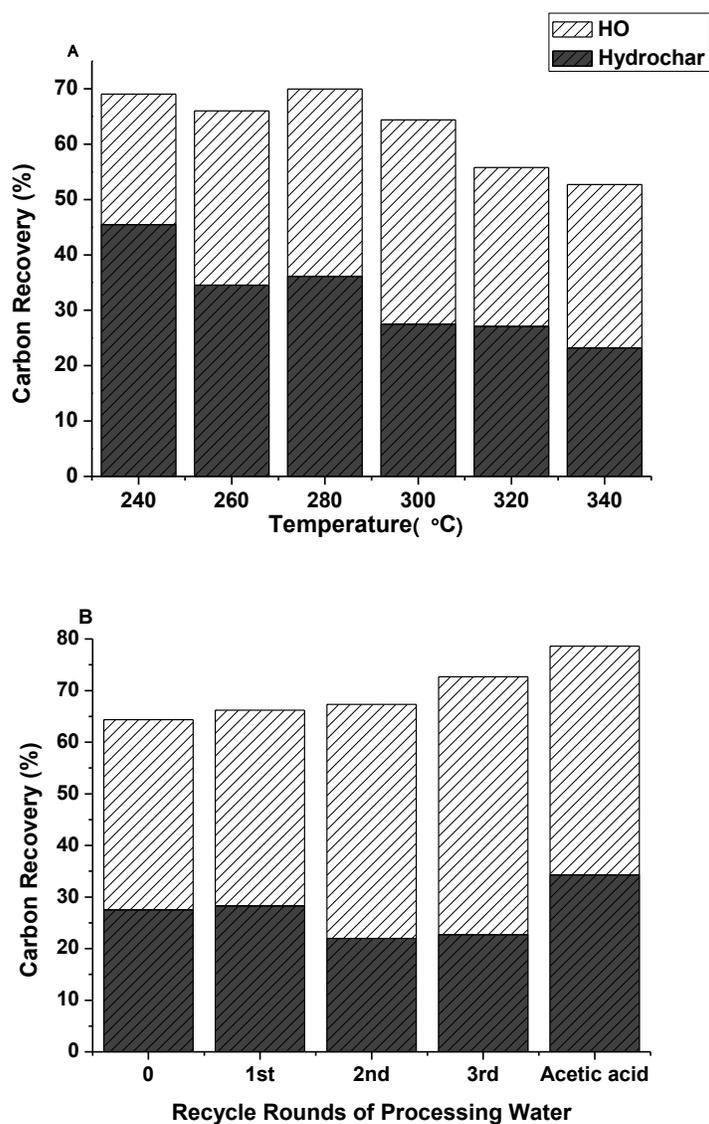


Fig. 4. The carbon recovery of HO and HC obtained at different (A) temperatures and (B) recycling rounds of the processing water

CONCLUSIONS

1. *Salix psammophila* (SP) branch residues were converted into bio-oils with high value-added compounds and hydrochar through hydrothermal liquefaction. The recycling of the processing water had significant effects on product yields and properties.
2. From the GC-MS analysis, the bio-oils were mainly composed of phenolics, acetic acid, and furans. The percent of the total weight (boiling point < 300 °C) of bio-oils

was about 41 wt%. The highest yields of bio-oil and carbon recovery of HO were 46.87 wt% and 49.97%, respectively, which were obtained in the third recycling round of processing water. The total carbon recoveries of bio-oils and hydrochar may reach 80%.

3. The higher heating values (HHVs) of these HC were between 21 MJ/kg and 27 MJ/kg, which is equivalent to the heating value of medium-rank and high-rank coals according to the Chinese National Standard.
4. Based on the experimental results, the HTL of SP with the recycling of the processing water has great significance for the utilization of desert biomass waste.

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