Fuel Processing Technology 112 (2013) 93–99

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Thermochemical liquefaction of rice husk for bio-oil production in mixed solvent (ethanol–water)

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ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form 2 March 2013
Accepted 5 March 2013
Available online xxxx

Keywords:
Rice husk
Liquefaction
Ethanol–water
Bio-oil

ABSTRACT

Thermochemical liquefaction characteristics of rice husk in mixed solvent (ethanol–water) were investigated in this study. Compared with pure water or ethanol, the mixed solvent showed synergistic effect at a relatively lower temperature. The highest bio-oil yield was obtained at 533 K in ethanol–water mixed solvent (V/V, 5:5) and found to be 21.15%. In pure water and mixed solvent treatments, the yield of bio-oil declined with reaction temperature increasing from 533 K to 613 K. However, with the pure ethanol as solvent, the bio-oil yield increased firstly and then decreased slightly. In addition, the effects of solid–liquid ratio and solvent filling ratio on the distribution of liquefaction products were also explored with ethanol–water mixed solvent as medium. Higher solid–liquid ratio resulted in lower bio-oil yield, while the increase of solvent filling ratio led to an increase in the bio-oil yield. The compositions of bio-oil from rice husk consisted mainly of phenolic compounds, long-chain alkanes, ketones and esters. Compared with pure water or ethanol, the relative concentration of phenolic compounds in mixed solvent run was higher and reached up to 21.22%.

1. Introduction

With the increasing consumption of fossil fuels and the growing concerns about climate change, biomass is drawing increasing attention as a renewable energy source due to its advantages of renewal and abundance [1]. Currently, many first generation bio-fuels are derived from food crops. Therefore it is necessary to develop second generation bio-fuels that are not based on food crops [2]. One such feedstock is lignocellulosic biomass. There has been a plethora of research on the efforts to use various lignocellulosic biomass resources as feedstock to produce bio-fuel and/or value-added chemicals from hydrothermal process [1,3].

Rice is one of the most widely cultivated agricultural crops in China. The worldwide annual rice husk output is about 80 million tons with an annual energy potential of 1.2×10^9 GJ, corresponding to a heating value of 15 MJ/kg. In China, approximately 54 million tons of rice husk is produced every year. Rice husk is used to being produced massively at rice mills. Some of them are larger mills capable of processing 10–20 tons/h [4]. The high volumes of rice husks that are considered as waste after milling are not appropriately treated. If an efficient method is available, the rice husk can be converted to useful energy to help mitigate the overuse of fossil fuels.

Hydrothermal liquefaction is a low temperature and high pressure thermochemical process during which biomass is broken down into fragments of small molecules in water. These light fragments, which are unstable and reactive, can then re-polymerize into oily compounds with various ranges of molecular weights [5]. There has been a surge of interest in using hot-compressed and sub-/super-critical fluids for biomass liquefaction [1,6,7]. A great many of solvents have been used during this kind of treatment, such as water, ethanol, methanol, acetone and 1, 4-dioxane. Among these used solvents, water is the most environmental friendly. The presence of a moderate amount of water is considered to be effective for the production of oil fractions. However, Li et al. [8] proposed that in the liquefaction of biomass bio-oil fractions obtained in water have a lower carbon content and higher oxygen content, with a lower heating value. To enhance the yield of liquid products with lower oxygen content (hence higher heating value), the use of organic solvents has been adopted [8–10]. For one thing, solvent has remarkable effect on the liquefaction reaction [11]. For another, it has been proved that ethanol–water co-solvent would produce synergistic effect in biomass thermochemical liquefaction [3,12,13]. Also, it could be concluded that the physicochemical characteristic of sub/-super critical ethanol has many advantages [9,14], such as: 1. sub/-super critical fluids possesses unique transport properties (gas-like diffusivity and liquid-like density) and have complete miscibility with the liquid/vapor products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions; 2. sub/-super critical fluids have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/

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http://dx.doi.org/10.1016/j.fuproc.2013.03.005

liquefaction reactions; and 3. sub- and supercritical ethanol would also act as effective hydrogen donor by hydride transfer of their α-hydrogen through a so-called "hydrogen shuttling" mechanism. In view of above facts, ethanol–water mixed solvent was selected as liquefaction solvent to recover bio-oil products from rice husk.

To the best of our knowledge, liquefaction of rice husk has been reported, and Karagöz1's work in 2005 was a related study. Karagöz et al. [10] investigated the distribution of products, i.e. liquid, gas and solid from rice husk produced by hydrothermal treatment (553 K for 15 min) with water as solvent. It is significantly necessary that more efforts should be made to study the potential of rice husk as bio-fuel through liquefaction process. Therefore, the liquefaction characteristics of rice husk in mixed solvent (ethanol–water) were explored in this study. The influences of reaction parameters on both product yield and bio-oil compositions were investigated, such as reaction temperature (T), ethanol–water ratio (R_1), solid–liquid ratio (R_2) and solvent filling ratio (R_3).

2. Methods

2.1. Feedstock

Rice husks used as the biomass feedstock in this study were supplied from a rice mill in Hunan Province, China. And those rice husk samples with proper particle size ranging within 0.2–1.0 mm were selected for bio-oil production using thermochemical liquefaction. The proximate and ultimate analysis results of the rice husk sample are given in Table 1.

2.2. Thermochemical liquefaction procedure

Thermochemical liquefaction experiments have been carried out in a 500 mL GSHA-0.5 type autoclave which was obtained from Xintai Chemical Machinery Co., Ltd. (Weihai, China) and designed to a maximum temperature and pressure of 723 K and 30 MPa, respectively. A temperature controller provided by autoclave engineers was used to control operating temperatures. The controller was equipped with a Proportional-Integral-Differential (PID) control and safety features to prevent overheating. A water loop was installed for rapid cooling upon completion of the heating cycle. In each experiment, the reactor was loaded with a certain amount of rice husk and solvent. The reactants were agitated vertically using stirrer. The temperature was then raised to the desired levels (533 K, 573 K and 613 K) and maintained for 20 min. Afterwards, it was cooled down to the room temperature by fan and cool water. The experimental errors for the liquefaction yields and rice husk conversion are lower than 5% by three runs repeatedly at the same conditions.

2.3. Separation and extraction procedures

The procedures for separation and extraction of thermochemical liquefaction products are shown in Fig. 1. The solid and liquid products were rinsed from the autoclave by washing with proper amount of distilled water. Solid and liquid products were separated by filtration under a vacuum. The liquid potion was put in the rotary evaporator first to get rid of the residual ethanol. In the process of rotary evaporation, the vacuum degree was −0.09 MPa and the final temperature was up to 85 °C (the retention time was 15 min). Under this condition, the residual ethanol has already been evaporated, and then the liquid portion left in the flask was extracted with an adequate quantity of diethyl ether. The ethereal solution thus obtained was evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this portion was remained in the flask as part of bio-oil. The remaining solid products on the filter paper and the autoclave were washed with diethyl ether. After removing the diethyl ether under reduced pressure in a rotary evaporator, this fraction was in the same flask mentioned above as the other part of bio-oil. The two parts together were quantified and labeled as bio-oil. The remaining solids from the filter paper were named as solid residue (SR, diethyl ether insoluble fraction). This fraction was dried at 378 K and quantified.

2.4. Analysis

The bio-oils were analyzed by a gas chromatograph mass spectrometer (GC-MS). The analyses were conducted on a GCMS-QP2010 Plus spectrometer (Shimadzu, Japan) equipped with RTX-5MS capillary column (5% biphenyl 95% dimethyl polysiloxane, 30 m × 0.25 mm × 0.25 μm). He was adopted as the carrier gas. The flow rate of carrier gas He was 1.2 mL/min. The specific column temperature program of GC used in this study was as follows: 313 K (hold 3 min) → 463 K (12 K/min, hold 1 min) → 563 K (8 K/min, hold 20 min). The temperature of injection chamber was 543 K, and the temperature of transfer line was 553 K. In addition, the temperature of ion source was 503 K and the mass range was 40–450 m/z.

The raw material and bio-oil products were analyzed in terms of their elemental analysis using a CHNOS elemental analyzer (Vario EL III). The reported results are the mean values. The Higher Heating Values of biomass, and bio-oil were calculated according to the Dulong formula:

$$\text{Calorific value}(\text{MJ/kg}) = 0.3383\text{C} + 1.442(\text{H}-(\text{O}/8)) \qquad (1)$$

Table 1
Physicochemical characteristics of rice husk.

Proximate analysis[a]		Elemental analysis[c]	
Component	Content (wt.%)	Component	Content (wt.%)
Moisture	8.38	C	43.06
Combustibles[b]	76.85	H	6.08
Ash	14.77	N	4.26
		O[d]	46.60

[a] As received basis.
[b] Including volatile matter and fixed carbon.
[c] On a dry and ash free basis.
[d] Calculated by difference and assuming that the sulfur content is negligible.

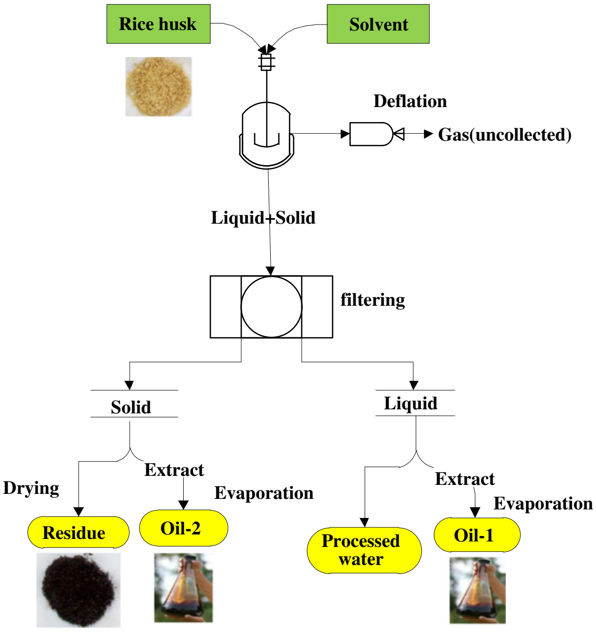

Fig. 1. Procedure for the separation of reaction products.

where C, H and O are the mass percentages of carbon, hydrogen, and oxygen, respectively.

2.5. Definition

The ethanol–water ratio (R_1) was defined as the percent of the volume of ethanol to that of water. The solid–liquid ratio (R_2, g/mL) was defined as the percentage of the mass of rice husk to the volume of solvent. The solvent filling ratio (R_3, %) was defined as the percentage of the volume of solvent to that of autoclave (500 mL).

The yield of each product (bio-oil and SR) and conversion rate is expressed in wt.% and calculated as follows:

$$\text{Yield of bio}-\text{oil} = (\text{mass of bio}-\text{oil})/(\text{mass of rice husk}) \times 100\% \quad (2)$$

$$\text{Yield of SR} = (\text{mass of SR})/(\text{mass of rice husk}) \times 100\% \quad (3)$$

$$\text{Conversion rate} = 100\%\text{–yield of SR}. \quad (4)$$

The gaseous products and the water formed during liquefaction process were not quantified, whereas they could clearly display the liquefaction degree of biomass. The total yield of gas and water was roughly estimated by difference assuming negligible mass loss for solvent during liquefaction process.

$$\text{Yield of}(\text{Gas}+\text{Water}) = 100\%\text{–yield of bio}-\text{oil–yield of SR} \quad (5)$$

3. Results and discussion

3.1. Effect of ethanol–water ratio (R_1) and reaction temperature (T)

Fig. 2 displays the product distributions from the thermochemical liquefaction of rice husk at temperatures of 533 K, 573 K and 613 K with different ethanol–water ratios (R_1 = 0:10, 5:5 and 10:0). The solid–liquid ratio (R_2) and solvent filling ratio (R_3) were fixed at 0.079 g/mL and 20%, respectively. The yields of bio-oil, solid residue and gas/water were in the range of 6.59–21.15%, 10.69–49.09% and 32.42–82.72%, respectively. The final pressures of reactions were in the range of 4–15 MPa.

3.1.1. Effect of ethanol–water ratio (R_1)

As shown in Fig. 2, the increase of ethanol–water ratio brought on an increase in the yield of bio-oil at 573 K and 613 K. Being different from the higher temperatures (573 and 613 K), at the relative low temperature 533 K (less energy consumption), the increase of the ethanol–water ratio from 0:10 to 5:5 brought about an increment in bio-oil yield but a decrease of that when ethanol–water ratio was further promoted to 10:0. This fact meant that the highest bio-oil yield at 533 K was found in ethanol–water mixed solvent (R_1 = 5:5). In other words, ethanol and water showed synergistic effects on the direct liquefaction of rice husk at this temperature. This phenomenon was consistent with a former study where the authors suggested that the optimal ethanol–water volume ratio for cellulose hydrothermal degradation was 5:5 [15].

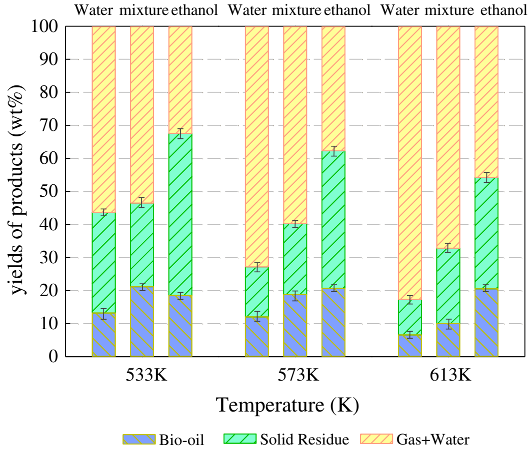

Fig. 2. Effect of reaction temperature (T) and ethanol–water ratio (R1) on the liquefaction production distribution.

The critical temperature of the ethanol–water co-solvent (R_1 = 5:5) is about 587 K [16], apparently, the liquefaction process was carried out under the sub- and supercritical conditions in this study. The hydrogen-donor capability of ethanol was promoted in the sub-/supercritical condition [16]. On the one hand, water could lead to high bio-oil yield, but that decreased at the higher water amount for the formation of solid residue (SR) through self-condensation reactions [1]. Also, hot-compressed water has been found very effective for promoting ionic, polar non-ionic and free-radical reactions [13]. On the other hand, ethanol, as extraction solvent, has much higher dissolving power for oils [17]. The adding ethanol could act as both reaction substrate and hydrogen-donor in the liquefaction process [9]. The combination of these advantages may prevent the formation of residue and improve the bio-oil yield. In addition, Chen et al. [12] proposed that the excessive ethanol content could bring on the decrement of free-radical for its weak acidity, which is not conducive to biomass liquefaction and resulted in the bio-oil yield reduce. A mechanism was proposed in earlier literature [16] that ethanol had a hydrogen-donor capability to stabilize the free radicals generated and thus reduce the repolymerization reaction, finally, low-boiling-point materials were produced which might be vaporized and vented in the rotary evaporator. With proper amount of water, ethanol was diluted by it, and the formation of high-boiling-point materials (labeled as bio-oil) was promoted. Former works [15,16] have reported that the critical point and the dielectric constant of the alcohol/water mixture would be lower than that of pure water, which led to milder conditions for the reaction and the increase of the solubility of relatively high molecular weight products from cellulose, hemicelluloses, and lignin. All these aspects mentioned above demonstrate that ethanol–water co-solvent is a better choice than a sole one at relative low temperatures. And these were the reasons that the highest bio-oil yield was obtained in ethanol–water mixture.

The solid residue (SR) yields decreased sharply with the ethanol–water ratio decreasing from 10:0 to 0:10 at higher temperatures (573 and 613 K). Hot-compressed water appeared to be more active than ethanol for the conversion of rice husk. Previous studies [10,18,19] related to hydrothermal liquefaction of biomass also showed that water favors the biomass conversion. However, when temperature was at 533 K the yields of solid residue with ethanol–water (10:0 and 0:10) treatments were higher than that in ethanol–water run with the ratio of 5:5. In other words, using the mixture can promote the conversion of rice husk in contrast to pure water and pure ethanol at 533 K. Ye et al. [3] reported that compared to pure water or ethanol, the ethanol–water mixture could effectively inhibit condensation, gasification and dehydration of lignin to help decrease the SR yield.

3.1.2. Effect of reaction temperature (T)

In this study, slightly higher temperatures from 533 to 613 K were tested for rice husk direct liquefaction for the production of bio-oils. The effects of reaction temperature on the yields of bio-oil, SR, and gas/water from liquefaction are shown in Fig. 2. The results clearly display that the yields of bio-oil obtained from ethanol–water (R_1 = 0:10, 5:5) treatments continuously decreased, while in the pure ethanol treatment (R_1 = 10:0), the bio-oil yield increased firstly and then declined slightly. Fig. 2 also shows that in the pure solvent (pure water or ethanol), SR yield decreased with increasing reaction temperature, while with the ethanol–water mixture (R_1 = 5:5), the

SR yield decreased from 533 K to 573 K and increased from 573 K to 613 K. Additionally, the gas/water yield increased with the increment of reaction temperature.

It has been reported that when biomass was heated in liquid water, solvolysis of hemicellulose and lignin began to occur at > 190 °C and all of the hemicellulose and much of the lignin dissolved in the water at 220 °C, forming the intermediates or products. Solvolysis and pyrolysis of the remaining lignocellulosic solids took place at higher temperatures. The intermediate products of these solvolysis and pyrolysis reactions could go through an extraordinary variety of reactions such as cyclization, polymerization, isomerization, dehydration, fragmentation, and condensation reactions that ultimately formed gas, bio-oils, and char [8,18–20]. The greatly reduced bio-oil at 613 K in pure water treatment may be explained by the formation of hydrocarbon gasses through cracking reactions of the bio-oil. Just as the previous paper [20] indicated as the temperature was promoted to or beyond the critical point of water, gasification becomes the dominating process. This assertion may be evidenced by the results in Fig. 2, showing the yields of gas/water increased as temperature increased from 533 K to 613 K.

As revealed in Fig. 2, pure ethanol treatment had different patterns from pure water treatment. The reason may be that compared with water, alcohols with longer alkyl chains could dissolve macromolecules and liquefy lignocelluloses rapidly in supercritical region (ethanol, T_c: 513.8 K, P_c: 6.1 MPa; water, T_c: 647 K, P_c: 22 MPa) [15]. Furthermore, ethanol can react with the decomposition intermediates, especially at higher temperatures, to promote bio-oil formation and prevent SR formation from the decomposition intermediates [12]. Li et al. [21] had earlier proposed that ethanol could react with the free radicals produced from the decomposition of sludge. Considering the different variations of bio-oils from the pure ethanol and pure water solvents, it was clear that with the increment of reaction temperature, ethanol could take more activity in the reactions to attain more bio-oils. This conclusion was consistent with the former studies [9,11]. The variation of bio-oil from ethanol–water ($R_1 = 5{:}5$) treatment was attributed to the combination effects of the varying patterns from pure water and ethanol treatments.

3.2. Effect of solid–liquid ratio (R_2) and solvent filling ratio (R_3)

Fig. 3 presents the yields of products from the liquefaction of rice husk in ethanol–water mixture ($R_1 = 5{:}5$) at a fixed temperature (533 K) with different R_2 (0.039–0.118 g/mL) and R_3 (10%–30%). The lowest bio-oil was obtained at the highest S/L ratio (0.118 g/mL) with a low solvent filling ratio of 10%. The highest bio-oil yield was found to be 31.5% at 0.079 g/mL with a high solvent filling ratio of 30%. The final pressures of reactions were in the range of 4–6 MPa.

3.2.1. Effect of solid–liquid ratio (R_2)

It can be found from Fig. 3 that the bio-oil yields decreased with the increasing solid–liquid ratio at 10% and 20% solvent filling ratio. However, at 30% solvent filling ratio, the yield of bio-oil increased firstly and then reduced. A lower biomass concentration or a higher solvent content prevailed through the whole process, which might thus facilitate the solvolysis, hydrolysis and hydration of the lignocellulosic solids, leading to a higher yield of bio-oil, gas/water and a smaller yield of solid residue [13]. Furthermore, a well-mixed suspension could be formed in the reactor, which helps the conversion of rice husk to products.

The major functions of solvent were decomposing biomass, dissolving relatively high molecular weight products, diluting the concentration of the products to prevent the cross linked or reverse reactions and acting as hydrogen-donor during the liquefaction process [11,12,22]. Increasing R_2 implied that the amount of rice husk was increased, but the relative amount of liquefaction solvent was reduced. In other words, the functions of solvent were relatively weakened. Another possible

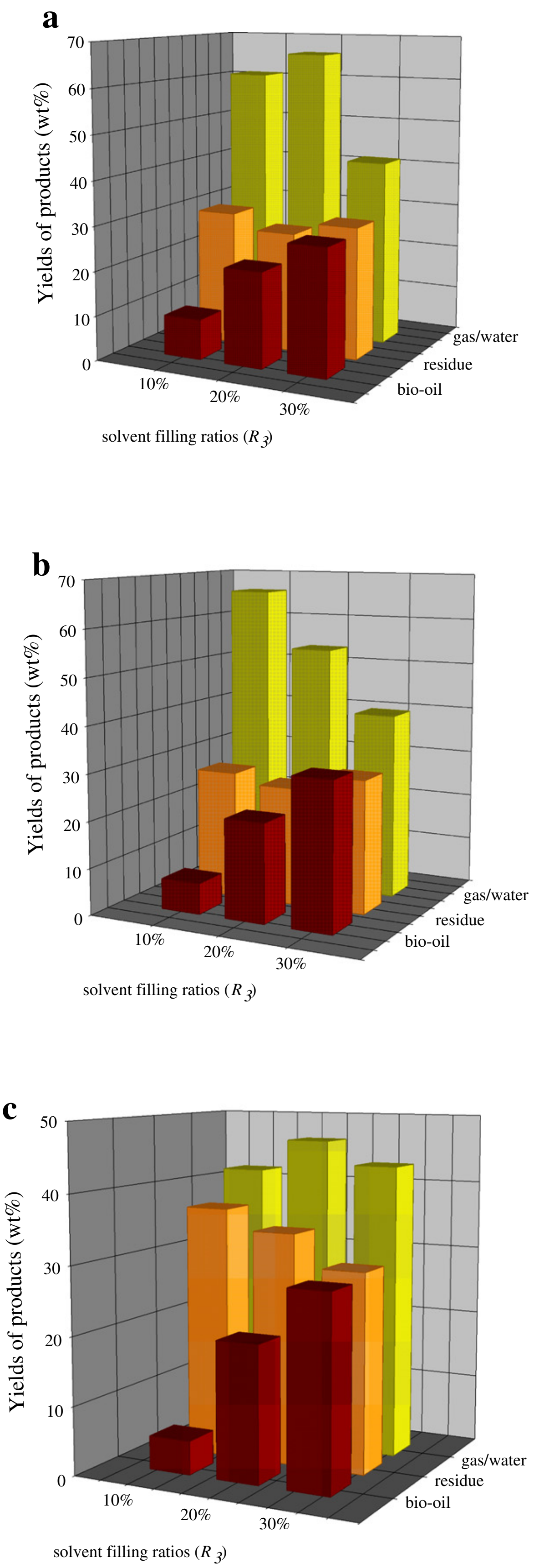

Fig. 3. The product distributions from the hydrothermal liquefaction of rice husk. (a) $R_2 = 3.95$ g/mL, (b) $R_2 = 7.89$ g/mL, (c) $R_2 = 11.84$ g/mL.

reason could be the formation of char by condensation reactions of bio-oil intermediates/products at a high S/L ratio [11]. Cheng et al. [13] also proposed that a handful of solvent will prevent the liquefaction and solvolysis reactions. Therefore, the bio-oil yield would be reduced when R_2 was beyond the optimum point.

3.2.2. Effect of solvent filling ratio (R_3)

According to Fig. 3, the yield of bio-oil increased rapidly with R_3 increasing from 10% to 30%. As regards the yield of solid residue, a decline trend was observed firstly, and then a rising phenomenon appeared at lower S/L ratios ($R_2 = 0.039$ and 0.079 g/mL). Being at a higher S/L ratio ($R_2 = 0.118$ g/mL), the SR decreased continuously with increasing solvent filling ratios. A different trend was observed for the yield of gas/water at lower S/L ratios ($R_2 = 0.039$ and 0.079 g/mL). The yield of gas/water decreased with R_3 increasing from 10% to 30%. But at a higher S/L ratio ($R_2 = 0.118$ g/mL) an increment of gas/water yield could be observed with R_3 increasing from 10% to 20%, and further increasing R_3 led to a decrease in gas/water yield.

A higher R_3 meant more liquefaction solvent. As the amount of liquefaction solvent was increased, the functions of solvent were enhanced [9]. Pressure also increased as the increment of R_3, which results in intensified decomposition and extraction [23]. The condensation, cyclization and re-polymerization of the intermediates and liquid products were prevented owing to the increment of pressure [9]. Hence, the formations of SR and gas/water were slightly restrained. This assertion may be evidenced by the results shown in Fig. 3 that the yields of gas/water decreased at higher solvent filling ratio. Therefore, it was easy to understand that the yield of bio-oil increased with the increment of the solvent filling ratio and the yield of residue decreased at higher solvent filling ratio.

3.3. GC-MS analysis

The bio-oils collected contained a complex mixture of hydrocarbons and has been analyzed by GC/MS. The identification of the main compounds was performed using a NIST mass spectral database. Tables 2–4 give a comparison of the identified compounds in the bio-oils from liquefaction of rice husk at 533 K with different ethanol–water ratios ($R_1 = 0{:}10, 5{:}5, 10{:}0$). The area (%) for each compound identified was defined by percentage of the compound's chromatographic area out of the total area. Only those compounds with area (%) higher than 1% were presented in these tables.

According to Table 2, it is clearly seen that phenolic compounds (18.55%) are the major compounds identified in the bio-oil obtained from liquefaction of rice husk in pure water ($R_1 = 0{:}10$), followed by ketones (11.27%), long-chain alkanes (10.4%), esters (8.14%), and aldehydes (6.15%). In the case of ethanol–water mixed solvent treatment (Table 3), the main components of bio-oil are phenolic compounds (21.22%), and the contents of long-chain alkanes (12.8%), esters (7.32%), organic acids (6.72%), and ketones (6.12%) are the next. As shown in Table 4, as regards pure ethanol treatment ($R_1 = 10{:}0$), the main compounds of bio-oils are saccharides (18.49%), phenolic compounds (16.28%), esters (12.74%), furans (5.42%) and ketones (3.67%).

Compared with pure water or ethanol, the ethanol–water mixed solvent produced the highest yield of phenolic compounds, which suggested that mixed solvent could promote the formation of phenolic compounds. Akalin et al. [6] reported that phenolic compounds could be formed from the decomposition of furfural and furfural derivatives. Also, the phenolic compounds could be originated from the degradation of the lignin component in risk husk [14]. From the researches of wood chemistry [24,25], lignin has phenyl propane units, which are highly rich sources of phenolic compounds. When using mixed solvent as reaction solvent, the water could act as a nucleophile and reacted with some

Table 2
Major chemical compositions of bio-oils obtained in pure water run.

No.	RT (min)	Name of compounds	Area (%)
1	8.39	Phenol (C_6H_6O)	1.45
2	8.48	1,2-Dimethoxy-4-(1-methoxyethenyl)benzene ($C_{11}H_{14}O_3$)	1.9
3	9.07	1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	3.35
4	9.47	Pentanoic acid, 4-oxo- ($C_5H_8O_3$)	1.61
5	9.98	Phenol, 2-methoxy- ($C_7H_8O_2$)	1
6	10.07	Undecane ($C_{11}H_{24}$)	2.12
7	10.12	Tridecane ($C_{13}H_{28}$)	1.31
8	10.24	3-Pyridinol (C_5H_5NO)	5.47
9	10.97	Phenol, 4-ethyl- ($C_8H_{10}O$)	1.28
10	11.10	Phenol, 3-ethyl- ($C_8H_{10}O$)	1.13
11	11.42	Dodecane ($C_{12}H_{26}$)	1.77
12	11.52	1,2-Benzenediol ($C_6H_6O_2$)	3.63
13	11.92	2-Furancarboxaldehyde, 5-(hydroxymethyl)- ($C_6H_6O_3$)	2.47
14	12.81	Tetradecane ($C_{14}H_{30}$)	2
15	13.39	1,4-Benzenediol, 2-methyl- ($C_7H_8O_2$)	1.33
16	13.56	Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)	1.36
17	14.00	Vanillin ($C_8H_8O_3$)	1.33
18	14.03	Ethanone, 1-(3-hydroxyphenyl)- ($C_8H_8O_2$)	1.03
19	14.07	Pentadecane ($C_{15}H_{32}$)	1.15
20	14.18	Benzaldehyde, 3-hydroxy-4-methoxy- ($C_8H_8O_3$)	2.35
21	14.56	Acetophenone, 4′-hydroxy- ($C_8H_8O_2$)	1.16
22	15.20	5-Hepten-3-yn-2-ol,6-methyl-5-(1-methylethyl)- ($C_{11}H_{18}O$)	2.08
23	15.68	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	1.29
24	18.22	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- ($C_{10}H_{12}O_4$)	1.39
25	19.07	Phenanthrene ($C_{14}H_{10}$)	1.02
26	20.62	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione ($C_{17}H_{24}O_3$)	1.35
27	20.85	Pyrrolo[1,2-a]pyrazine-1,4-dione,hexahydro-3-(2-methylpropyl)- ($C_{11}H_{18}N_2O_2$)	1.7
28	20.94	n-Hexadecanoic acid ($C_{16}H_{32}O_2$)	3.59
29	21.10	Dibutyl phthalate ($C_{16}H_{22}O_4$)	8.14
30	30.55	Squalene ($C_{30}H_{50}$)	1.03

Table 3
Major chemical compositions of bio-oils obtained in ethanol- water run.

No.	RT (min)	Name of compounds	Area (%)
1	5.26	Benzoylformic acid ($C_8H_6O_3$)	1.07
2	8.41	Phenol (C_6H_6O)	1.83
3	8.5	1,2-Dimethoxy-4-(1methoxyethenyl)benzene ($C_{11}H_{14}O_3$)	1.55
4	9.10	1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	3.49
5	9.47	Pentanoic acid, 4-oxo- ($C_5H_8O_3$)	1.96
6	9.56	Pentanoic acid, 4-oxo-, ethyl ester ($C_7H_{12}O_3$)	1.49
7	9.76	Phenol, 4-methyl- (C_7H_8O)	1.03
8	10.01	Phenol, 2-methoxy- ($C_7H_8O_2$)	3.73
9	10.10	Undecane ($C_{11}H_{24}$)	1.5
10	10.14	Undecane, 3,9-dimethyl- ($C_{13}H_{28}$)	1.07
11	10.25	3-Pyridinol (C_5H_5NO)	4.18
12	10.40	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	1.61
13	11.00	Phenol, 4-ethyl- ($C_8H_{10}O$)	2.27
15	11.10	Phenol, 3-ethyl- ($C_8H_{10}O$)	1.84
17	11.45	Dodecane ($C_{12}H_{26}$)	1.18
18	11.52	1,2-Benzenediol ($C_6H_6O_2$)	3.84
19	11.92	2-Furancarboxaldehyde, 5-(hydroxymethyl)- ($C_6H_6O_3$)	1.43
20	12.39	cis-3-Hexenoic acid ($C_6H_{10}O_2$)	1.29
21	12.73	Tridecane ($C_{13}H_{28}$)	1.52
22	12.83	Tetradecane ($C_{14}H_{30}$)	3.03
23	13.41	Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)	1.4
24	13.56	Phenol, 3,4-dimethoxy- ($C_8H_{10}O_3$)	1.3
25	13.96	Eicosane ($C_{20}H_{42}$)	1.27
26	14.04	Hexadecane ($C_{16}H_{34}$)	3.23
27	14.18	Vanillin ($C_8H_8O_3$)	1.41
28	14.76	Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	1.4
29	15.10	Oxalic acid, heptyl 2-isopropylphenyl ester ($C_{18}H_{26}O_4$)	1
31	15.69	2-Propanone,1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	1.02
32	20.94	n-Hexadecanoic acid ($C_{16}H_{32}O_2$)	2.4
33	21.10	Dibutyl phthalate ($C_{16}H_{22}O_4$)	4.83
34	28.93	1,1′-Biphenyl-3,4,4′-trimethoxy-6′-formyl- ($C_{16}H_{16}O_4$)	1.02

Table 4
Major chemical compositions of bio-oils obtained in ethanol run.

No.	RT (min)	Name of compounds	Area (%)
1	6.7	2-Furanmethanol ($C_5H_6O_2$)	2.05
2	8.42	Phenol (C_6H_6O)	1.45
3	9.11	1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	1.14
4	9.46	Ethyl 5-methylhexanoate ($C_9H_{18}O_2$)	1.07
5	9.57	Pentanoic acid, 4-oxo-, ethyl ester ($C_7H_{12}O_3$)	1.48
6	9.76	dl-Leucine, N-[(phenylmethoxy)carbonyl]- ($C_{14}H_{19}NO_4$)	1.26
7	9.84	Furan, 2-butyltetrahydro- ($C_8H_{16}O$)	2.55
8	10.03	Phenol, 2-methoxy- ($C_7H_8O_2$)	3.22
9	10.10	Octane, 2,4,6-trimethyl- ($C_{11}H_{24}$)	1.02
10	11.02	Phenol, 4-ethyl- ($C_8H_{10}O$)	2.26
11	11.07	Phenol, 3-ethyl- ($C_8H_{10}O$)	1
12	11.44	Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	2.02
13	11.53	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl- ($C_9H_{14}O$)	2.53
14	12.44	Butanoic acid, 2-propenyl ester ($C_7H_{12}O_2$)	2.27
15	12.56	Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	2
16	12.64	5-Isopropyl-3,3-dimethyl-2-methylene-2,3-dihydrofuran ($C_{10}H_{16}O$)	1.24
17	12.68	Benzene, 1,4-dimethoxy-2-methyl- ($C_9H_{12}O_2$)	1.75
18	13.56	Beta.-D-riboside ethyl ($C_7H_{14}O_5$)	4.09
19	13.65	Phenol, 2-methoxy-4-propyl- ($C_{10}H_{14}O_2$)	1.27
20	13.79	Homovanillyl alcohol ($C_9H_{12}O_3$)	1.44
21	13.97	.Beta.-D-ribopyranoside, methyl ($C_6H_{12}O_5$)	3.42
22	14.07	1,2,4,5-Cyclohexanetetrol,(1.alpha,2.alpha,4.alpha,5.beta)- ($C_6H_{12}O_4$)	1.63
23	14.56	Alpha.-D-lyxofuranoside, methyl ($C_6H_{12}O_5$)	1.27
24	14.63	2-Pyrrolidinecarboxylic acid-5-oxo-, ethyl ester ($C_7H_{11}NO_3$)	3.11
25	14.77	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- ($C_{10}H_{12}O_2$)	1.31
26	15.20	Beta.-D-glucopyranose, 1,6-anhydro- ($C_6H_{10}O_5$)	5.03
27	16.69	Alpha.-D-glucopyranoside ethyl ($C_8H_{16}O_6$)	2.62
28	16.84	Beta.-D-glucopyranoside, methyl ($C_7H_{14}O_6$)	2.06
29	17.09	Benzenepropanoic acid, 4-hydroxy-, methyl ester ($C_{10}H_{12}O_3$)	1.65
30	18.41	Ethyl-.beta.-(4-hydroxy-3-methoxy-phenyl)-propionate, ($C_{12}H_{16}O_4$)	1.03
31	21.38	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	1.57
32	23.51	Ethyl oleate ($C_{20}H_{38}O_2$)	1.63

active centers in the proto-lignin [8]. Ye and Chang [3] also proposed that ethanol–water mixed solvent showed synergistic effects on lignin hydrothermal degradation.

The relative content of long-chain alkanes in the bio-oil obtained from mixed solvent treatment was 12.8% which was much higher than those from pure water or ethanol treatments. Therefore, a conclusion may be made that the formation of alkanes was also enhanced with ethanol–water mixture as liquefaction solvent. On the other hand, the content of ketones from pure water treatment was the highest, which may be obtained with adequate water via the retro-aldol condensation during the liquefaction of cellulose [8].

Now that sub/supercritical ethanol–water were weak acid, the rice husk liquefaction could be considered as an acid-catalyzed process [12]. Cellulose and other carbohydrates underwent dehydration to form mono-saccharides, a part of which may then react with ethanol to form the ether that exists in the solid residues. Most of the mono-saccharides may further react to generate carboxylic acid or other organic compounds under the acid-catalyzed process [26].

A lot of saccharides were found in bio-oil from pure ethanol treatment. When pure ethanol was selected as the liquefaction solvent, the critical temperature was about 516 K [16], and the actual liquefaction temperature (533 K) is very close to the critical point. Therefore, the liquefaction process was carried out under sub/supercritical condition. Toor et al. [20] proposed that at sub-/supercritical conditions cellulose was rapidly solubilized and hydrolyzed to its constituents and the cellulose hydrolysis was subsequently converted into monosaccharide and other products. Just as in the case of cellulose, the saccharides were released from hemicellulose and carbohydrates hydrolysis [26].

The ester content in bio-oil increased as the increase of ethanol–water ratio. This phenomenon may be related to two main reasons. In the first place, ethanol is an important hydrogen-donor solvent. Secondly, ethanol can react with amides and acids to form ethyl ester [9,12]. Most of the identified minor compounds were mainly found to be furans, acids and aldehydes. The furan derivatives and the acids were formed primarily from the cellulose and hemi-cellulose component of rice husk [14]. The small fragment aldehydes may be formed via the retro-aldol condensation during the liquefaction of cellulose without loss of water [8].

3.4. Elemental analysis

Table 5 shows the elemental compositions and the heating values (HHVs) of bio-oils obtained from rice husk liquefaction at 533 K with different ethanol–water ratios and a fixed R_2 (0.079 g/mL) and R_3 (20%). The elemental analysis results showed that all the bio-oils contained more carbon and hydrogen, but less oxygen and nitrogen than the raw material. However, sulfur was not observed in all products and the HHVs of bio-oils (as high as >25 MJ/kg) were found to be higher than that of the raw material (14.93 MJ/kg). Moreover, the O/C atomic ratio of bio-oils decreased, and the average value of bio-oils was decreased 76.85% than rice husk. As for the H/C atomic ratio, the average value of bio-oils was 8.57 times more than rice husk. These results may indicate that the deoxygenation has taken place during the liquefaction process [18]. It was probably owing to the fact that the oxygen content in bio-oil could decrease with the reduction of oxygen to water with hydrogen in the biomass and solvent [16].

As shown in Table 5, the ethanol–water ratio had an important effect on the HHV of bio-oils. The HHV of bio-oil increased with the increment of ethanol–water ratio from 0:10 to 10:0. This may be due to the fact that ethanol as hydrogen-donor solvent had contributed to the reduction of oxygen content of the bio-oils during sub/supercritical liquefaction: oxygen was combined with hydrogen in biomass and hydrogen-donor solvent to produce water and, consequently, the HHV of bio-oil increased [16]. In other words, the deoxygenation has been enhanced during liquefaction process. As Dulong formula, the HHV increases with the decreasing of oxygen content. Attention should also be paid to the fact that the HHVs of the bio-oils from mixed solvent and pure ethanol treatments were approximately the same (27.04 and 27.56 MJ/kg). Considering the low cost of water, ethanol–water mixed solvent could be a right choice instead of pure ethanol.

4. Conclusion

During the liquefaction of rice husk, the mixed solvent (ethanol–water) showed synergistic effect, which combined the advantages of

Table 5
Elemental analyses and other properties of bio-oils and rice husk obtained under different conditions.

Samples	Run				Elemental analysis (wt.%)				H/C atomic ratio	O/C atomic ratio	Heating value (MJ/kg)
	T (K)	R_1 (%)	R_2 (%)	Solvent	C	H	N	O[a]			
Rice husk	–	–	–	–	43.06	6.08	4.26	46.60	0.14	1.08	14.93
Bio-oil	533	7.89	20	Water	60.55	6.93	2.28	30.24	1.37	0.37	25.03
	533	7.89	20	Mixture	64.88	6.78	2.35	25.99	1.25	0.07	27.04
	533	7.89	20	Ethanol	63.63	7.46	2.68	26.23	1.41	0.31	27.56

[a] Calculated by difference and assuming that the sulfur content is negligible.

pure water and ethanol. Under tested conditions, the highest yield of bio-oil was obtained at 533 K with ethanol–water mixed solvent (V/V, 5:5) as medium. And the caloric value of bio-oil was 27.04 MJ/kg close to that in pure ethanol run. Higher solid–liquid ratio would impart negative effect on the production of bi-oil. But higher solvent filling ration would increase the yield of bio-oil. GC-MS analysis results showed that the main components of bio-oil obtained from ethanol–water mixed solvent run were phenolic compounds and esters.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No. 21276069 and No. 50978087) and the Hunan Province Innovation Foundation for Postgraduate (CX2012B139).

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