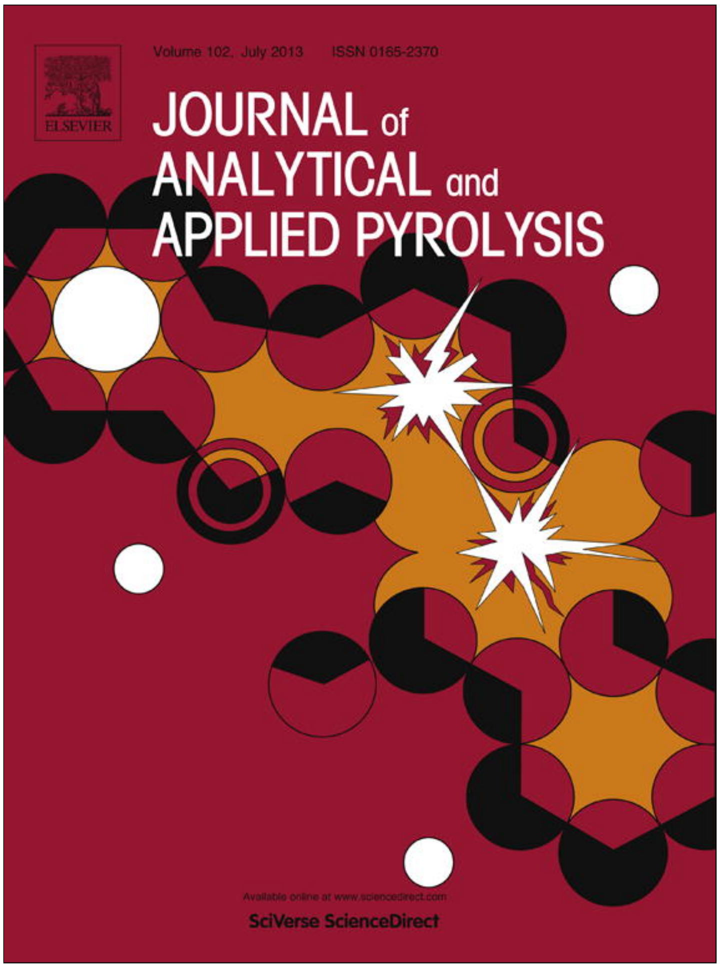

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Thermochemical liquefaction of rice husk for bio-oil production with sub- and supercritical ethanol as solvent

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ABSTRACT

Rice husk was converted into bio-oil via thermochemical liquefaction with ethanol as solvent in an autoclave (500 mL). The influences of reaction parameters on the yields of liquefaction products were investigated. Liquefaction experiments were performed at various reaction temperatures (T, 513–633 K), solid–liquid ratios (R_1, 5–15%), and solvent filling ratios (R_2, 10–30%) with or without catalyst. Two types of catalysts were involved, including iron-based catalysts ($FeSO_4$ and FeS) and alkali metal compounds ($NaCO_3$ and NaOH). The dosage of catalyst (R_3) was also optimized. Without catalyst, the bio-oil yields ranged from 11.8% to 24.2%, depending on T, R_1 and R_2. And the bio-oil yields increased firstly and then decreased with increasing T and R_2, while the bio-oil yields continuously declined with increasing R_1. NaOH was certified to be an ideal catalyst for rice husk liquefaction and the optimal dosage was approximately 10%. The obtained bio-oils had much higher caloric values of 20.9–24.8 MJ/kg compared to 14.9 MJ/kg for the crude rice husk sample. Without catalyst, the main components of bio-oil were phenolic compounds. In the case of NaOH as catalyst, long-chain alkanes were the major compositions of bio-oil.

1. Introduction

During the production of rice, rice husk is generated on site as a byproduct in the milling factory [1]. Annual production of rice husk is about 140 million tons worldwide. However, rice husk does not provide important use or commercial interest due to its high ash and lignin contents [2]. Traditional methods such as composting and incineration are not suitable to process these organic solid wastes. The reason is that they contain small concentrations of nitrogen for composting and a considerable amount of solid grains and smoke would be released to pollute the environment during incineration [3]. From a different perspective, rice husk may be a species of potential renewable energy resource. Utilization of rice husk in this way, instead of as waste, will mean less pollution [4]. Therefore, more efficient treatment methods satisfying both energy conversion and wastes disposal are required [5].

Recently, many efforts have been made to recover energy from rice husk through thermochemical technologies, such as direct combustion [6], gasification [7], pyrolysis [2,5,8–10] and liquefaction [11]. Studies on liquefaction of rice husk are however quite limited. In an earlier work, Karagöz et al. [11] investigated the distribution of products, i.e. liquid, gas and solid from rice husk produced by hydrothermal treatment (553 K for 15 min). And the compositional analysis results of liquid hydrocarbons (bio-oils) were also reported. To the best of the authors' knowledge, to date, few reports, if any, were issued on detailed liquefaction characteristics of rice husk under different reaction conditions, which is just the issue to be discussed in depth in the present paper.

Liquefaction of biomass with proper solvents is a process that can prospectively be integrated with optimized conditions to simultaneously produce fuel additives and valuable chemicals [12]. Ethanol has been widely adopted as solvent for liquefaction of various biomasses, including sewage sludge [13], microalgae [14,15] and lignocelluloses [16,17]. Ethanol has several advantages: first, the critical temperature and critical pressure of ethanol (516.2 K, 6.38 MPa) is far below that of water, so much milder reaction conditions can be obtained; second, ethanol can provide active hydrogen as a hydrogen-donor in the liquefaction process; third, ethanol can react with acidic components in the bio-oil by esterification

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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.

reaction to obtain fatty acid ethyl esters similar to biodiesel; finally, due to relatively lower dielectric constant, ethanol can readily dissolve relatively high-molecular weight products derived from biomass [18,19]. From the viewpoint of efficiency and reproducible ability, ethanol may be the most promising one for biomass liquefaction among all the supercritical organic solvents [12,20]. Therefore, ethanol was chosen as the reaction medium for rice husk liquefaction in this study.

The main object of this paper is to study the effects of various reaction parameters on the liquefaction characteristics of rice husk in sub- and supercritical ethanol. The liquefaction factors taken in to account included final reaction temperature (T), solid-liquid ratio (R_1), solvent filling ratio (R_2) and type, dosage of catalyst (R_3). The chemical compositions of bio-oils were determined by using gas chromatography–mass spectrometry (GC–MS). The elemental analysis of bio-oils and solid phase products (solid residue, SR) were also conducted.

2. Materials and methods

2.1. Materials and ***chemicals***

Rice husk used in the experiments was provided by a rice mill in Hunan Province, China. Sun dried sample, separated from physical impurities, was ground in a rotary cutting mill and was screened into fractions of particle diameter (d_p) between 0.2 and 0.9 mm. The powder was dried in an oven at 378 K for 24 h before use. The proximate and ultimate analysis results of the rice husk sample are given in Table 1. All chemicals of ethanol, acetone, NaOH, Na_2CO_3, FeS and $FeSO_4$ were analytical reagent grade and used as received. Anhydrous ethanol and acetone were supplied by Fuyu Fine Chemical Co., Ltd. (Tianjin, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), respectively. NaOH, Na_2CO_3 and $FeSO_4$ were purchased from Damao Chemical Reagent Factory (Tianjin, China), while FeS was provided by Kermel Chemical Reagent Co., Ltd. (Tianjin, China). The purity of all chemicals was higher than 99%, except for NaOH ($\geq$96%) and FeS ($\geq$85%).

2.2. Liquefaction apparatus and procedure

Hydrothermal liquefaction experiments were carried out in a batch stainless steel reactor (GSHA-0.5) equipped with a magnetic stirrer. The reactor was provided by Xintai Chemical Machinery Co., Ltd. (Weihai, China) with a volume capacity of 500 mL and designed to a maximum temperature and pressure of 723 K and 30 MPa, respectively. In a typical run, firstly, a certain amount of rice husk, ethanol and catalyst (if needed) mixture were loaded into the reactor. Secondly, the vessel was sealed and heated to the specified temperature by an external electric furnace. The temperature inside the reactor was monitored using a inner thermocouple and controlled by a proportional integral derivative module. Heating time was about 50–60 min. Then the temperature was maintained for 20 min. The reactants were agitated vertically at 75 rpm. After the desired reaction time was elapsed, the autoclave was cooled down to room temperature by cool water. Cooling time was about one hour.

2.3. Separation procedure

The procedure for separation of liquefaction products is shown in Fig. 1. Once the autoclave was cooled to room temperature, the gas inside was vented in a fume hood, and the solid/liquid products were rinsed from the autoclave by washing with acetone. The resulted suspension was filtered through a pre-weighed filter paper under vacuum to separate the solid and liquid products. The remaining solids from the filter paper were named as solid residue (SR, ethanol and acetone insoluble fraction). This fraction was dried in an oven at 378 K overnight and then quantified. By using a rotary vacuum evaporator (Senco R204B, China), the filtrate was evaporated under reduced pressure at 323 K to remove the solvents (ethanol and acetone), followed by being evaporated under reduced pressure at 363 K to remove the water formed during liquefaction process. The resulted liquid phase product was designated as bio-oil.

Yields of liquefaction products (bio-oil and SR) and conversion rate were all expressed in wt% and calculated as follows:

$$\text{Yield of bio-oil} = \frac{\text{Mass of bio-oil}}{\text{Mass of rice husk}} \times 100\% \tag{1}$$

$$\text{Yield of SR} = \frac{\text{Mass of SR}}{\text{Mass of rice husk}} \times 100\% \tag{2}$$

$$\text{Conversion rate} = 100\,\text{wt\%} - \text{yield of SR} \tag{3}$$

The gaseous products and the water formed during liquefaction process were not quantified. The total yield of gas and water was roughly estimated by difference (Eq. (4)) assuming negligible mass loss for ethanol during liquefaction process [19,21].

$$\text{Yield of(Gas+Water)} = 100\,\text{wt\%} - \text{yield of bio-oil} - \text{yield of SR} \tag{4}$$

All liquefaction experiments were repeated three times under nominally identical conditions to ensure the repeatability of the results. The maximum standard deviations of bio-oil and SR yields were both less than 5%.

2.4. Characterization

The elemental compositions (C, H, N and O) of raw material, bio-oil and solid residue products were analyzed by an Elementar Vario EL III analyzer (Germany). The composition of oxygen (O) was estimated by difference. Elemental analysis was conducted two times. The reported results are the mean values. The calorific value was calculated according to the Dulong formula [14,21]:

$$\text{Calorific value (MJ/kg)} = 0.3383\text{C}+1.442(\text{H}) - (\text{O}/8)) \tag{5}$$

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

GC–MS 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). Helium was adopted as the carrier gas. The flow rate of helium 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 in the 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.

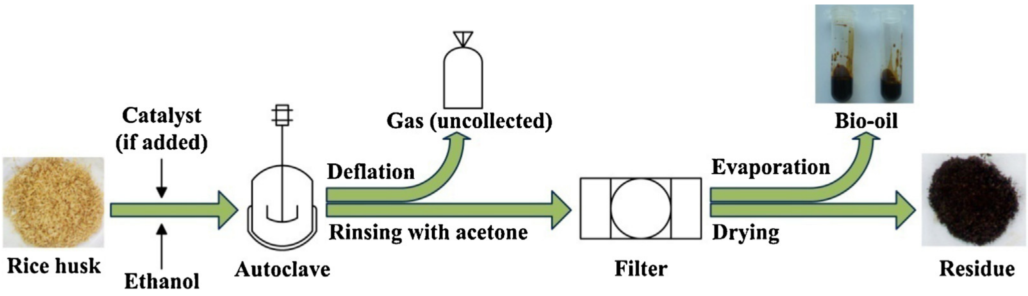

Fig. 1. Procedure for separation of liquefaction products.

2.5. Definition

The *S*/*L* ratio (R_1, %) was defined as the percentage of the mass of rice husk to that of ethanol. The solvent filling ratio (R_2, %) was defined as the percentage of the volume of ethanol to that of autoclave (500 mL). The dosage of catalyst (R_3, %) was defined as the percentage of the mass of catalyst to that of rice husk.

3. Results and discussion

3.1. Effect of reaction temperature (*T*)

The effects of reaction temperature (*T*) on the yields of liquefaction products can be inferred from Fig. 2, which presents the results obtained from the liquefaction operations at various temperatures ranging from 513 K to 633 K without catalyst. R_1 and R_2 were fixed at 10% and 20%, respectively. Over the whole range of the investigated temperatures, the SR yield was decreased monotonically with increasing temperature. However, a different trend was presented for the bio-oil yield. The bio-oil yield appeared to be maximized at approximate 593 K. When the reaction temperature was further elevated to 633 K, the yield of bio-oil was decreased slightly. The yield of (Gas + Water) showed an increase from 15.90% to 44.80% as the reaction temperature increased from 513 K to 633 K.

Biomass was firstly decomposed and de-polymerized to fragments of lighter molecules during the liquefaction process. And then these unstable fragments rearranged through condensation, cyclization and polymerization to form new compounds [14]. In general, the higher the reaction temperature, the easier the defragmentation of the polymers into a liquid oil-rich phase. A further increase of the reaction temperature leads to enhanced decomposition of these fragments into gaseous species. Below a critical temperature the former process (forming bio-oil) dominates the latter (forming gases). Above this critical temperature it is the other way round [22]. Akhtar and Amin [23] also proposed a similar viewpoint that the secondary decompositions and Boudouard gas reactions become active at high temperatures which lead to the formation of gases. In summary, a higher reaction temperature suggests enhanced decarboxylation, cracking/fragmentation, steam reforming/gasification and dehydration reactions of the intermediates/liquid/char products (to form gases and water) [24], as evidenced by the results of liquefaction product yields in Fig. 2.

3.2. Effect of the *S*/*L* ratio (R_1)

Fig. 3 illustrates the yields of liquefaction products (bio-oil and SR) at 573 K with different *S*/*L* ratios (5–15%). It is clearly shown in the figure that lower *S*/*L* ratio had positive impacts on the bio-oil yield. As the *S*/*L* ratio increased from 5% to 15%, the corresponding bio-oil yield decreased from 24.24% to 19.06%. Meanwhile, the SR yield increased with the increase of S/L ratio firstly, and then declined with the further elevation of *S*/*L* ratio.

During the liquefaction of biomass, solvents extract the biomass components, which can enhance the dissolution of biomass fragments. At high biomass to solvent ratios, the relative interactions among molecules of biomass and that of solvent become less influential, which can suppress the dissolution of biomass components [23]. Meanwhile, the active ethanol shared by unit mass of rice husk would be lowered with the increase of *S*/*L* ratio. In other words,

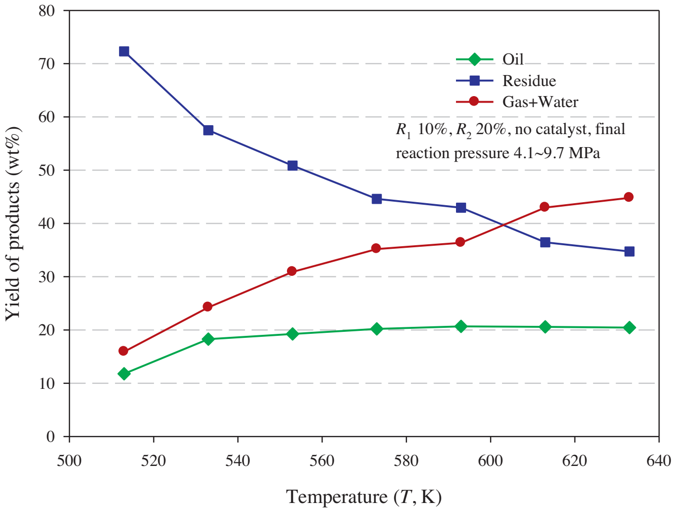

Fig. 2. Yields of bio-oil and SR varied with reaction temperature (*T*).

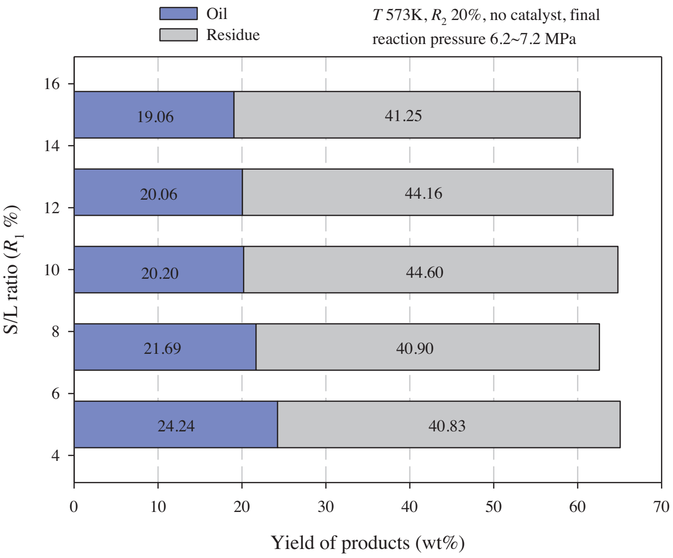

Fig. 3. Yields of bio-oil and SR varied with the *S*/*L* ratio (R_1).

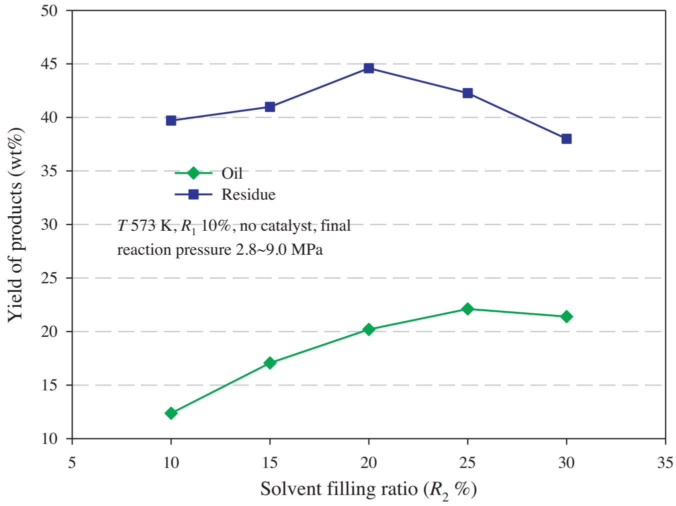

Fig. 4. Yields of bio-oil and SR varied with the solvent filling ratio (R_2).

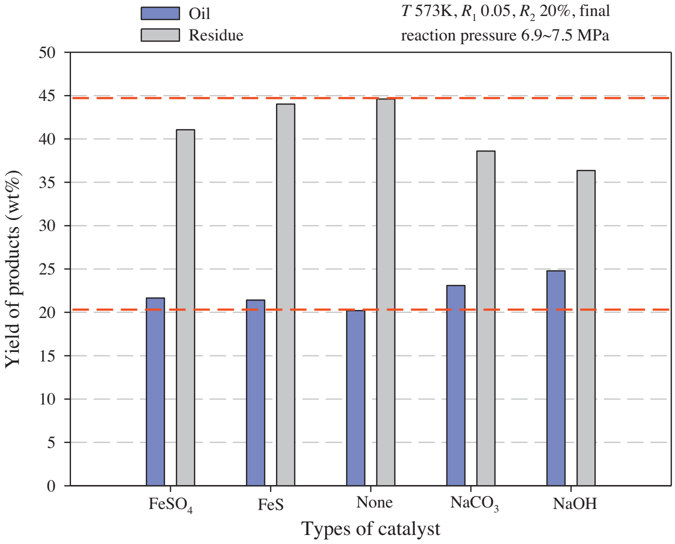

Fig. 5. Yields of bio-oil and SR varied with the type of catalyst.

the functions of solvent in enhancing the stability and solubility of fragmented components were relatively weakened. Therefore, the yield of bio-oil would decrease with increasing S/L ratio and the amount of leftover SR would increase.

Attention should also be paid to the fact that when the S/L ratio was further increased from 10% to 15%, the yield of SR declined. This may be ascribed to that more gas products were produced. Liquefaction process tends to behave like pyrolysis at very high biomass to solvent ratios. For comparison, pyrolysis of biomass usually produced more gases than liquefaction treatment [25]. Wang et al. [25] also observed that the amount of leftover residues were reduced at high solvent to biomass ratio. Apart from residues reduction, the gas yield was also decreased at high ratio of solvents [26].

3.3. *Effect of the solvent filling ratio (R_2)*

The effect of R_2 on the liquefaction characteristics of rice husk is depicted in Fig. 4. The data presented in this figure were obtained from the experiment runs at 573 K with different R_2 (10–30%) and a fixed R_1 (10%). According to Fig. 4, the yield of bio-oil increased quickly with the increase of R_2 firstly and then slightly declined. As regards the yield of SR, a rising trend was observed when the R_2 was lower than 20%. Further increasing R_2 resulted in an appreciable reduction. It was also found that R_2 had positive correlation with the final reaction pressure. The final reaction pressures approximately tripled when R_2 was increased from 10% to 30%.

Generally speaking, the higher the system pressure during liquefaction is, the less the liquid components will be gasified [22]. And the density of liquefaction solvent will increase with the elevating reaction pressure [13]. High-density medium penetrates efficiently into molecules of biomass components, which results in enhanced decomposition and extraction [23,27]. When the R_2 were set at 10 or 15%, the final reaction pressure were 2.8 MPa and 4.9 MPa, respectively. In other words, both liquefaction processes were conducted under subcritical conditions (critical point of ethanol: temperature 516 K, pressure 6.37 MPa). Therefore, it is not difficult to understand that the yield of bio-oil initially rose faster with increasing R_2.

However, once supercritical conditions for liquefaction are achieved, reaction pressure impart little or negligible influence on the yield of liquid oil. On the other hand, when the reaction pressure is further increased in supercritical conditions, cage effect will be caused, which ends up in low fragmentations [25]. This above-mentioned viewpoint may explain the phenomenon that the bio-oil yield was slightly reduced as the R_2 was further increased from 25% to 30%.

3.4. *Effect of the type and dosage of catalyst (R_3)*

A comparison of the yields of bio-oil and SR in the liquefaction of rice husk at 573 K, R_1 10% and R_2 20% with different catalysts is given in Fig. 5. On the whole, the addition of catalysts suppressed the formation of SR. In other words, the conversion rate of rice husk was increased. Especially in NaOH run, up to 63.64% of rice husk was converted. With iron-based compounds (FeS and $FeSO_4$) as catalysts, the yield of bio-oil was only slightly increased. But, in contrast, an obvious increase in bio-oil yield was obtained when alkali metal compounds (Na_2CO_3 and NaOH) were adopted as catalysts. Taking NaOH as an illustration, the yield of bio-oil was increased from 20.20% (without catalyst) to 24.79%.

Iron-based catalysts (such as FeS and $FeSO_4$) have been applied to catalytic liquefaction of various biomasses such as pine powder [21], sewage sludge [13] and microalgae [14]. These studies revealed that iron-based compounds were effective catalysts for biomass liquefaction. Li et al. [13] concluded that iron-based catalysts can improve the hydrogen transfer from hydrogen-donor solvent and/or biomass to the fragments derived from the decomposition of biomass, leading to stabilization of those fragments. Therefore, the addition of iron-based catalysts increased the yield of bio-oil.

Alkali metal compounds have also been widely employed as catalysts in direct liquefaction of agricultural/forest biomass to suppress the formation of char (residue) and to enhance the yield of liquid products [24]. As expected, the presence of NaOH and Na_2CO_3 in the liquefaction of rice husk both dramatically enhanced the organic conversion. At the same time, the bio-oil production was remarkably promoted. Furthermore, according to Fig. 5, the catalytic effect of NaOH was better than Na_2CO_3. The superior effect of NaOH for promoting bio-oil production and suppressing the formation of SR may suggest that NaOH can be a promising catalyst for catalytic liquefaction of rice husk using ethanol as solvent. The high activity of NaOH might be related to its strong alkalinity, facilitating the hydrolysis of polymers through the rupture the glycosidic bonds in cellulose and hemicellulose and the ester bonds in lignin [28].

However, a limitation of the results presented in Fig. 5 lies in the fact that they are from the operations at a fixed dosage of

Table 2
Elemental analyses and other properties of liquefaction products (bio-oil and SR) 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 (%)	Catalyst	C	H	N	O [a]			
Bio-oil	573	10	20	None	52.59	6.63	4.70	36.08	1.51	0.51	20.85
	573	10	20	NaOH	57.33	7.46	5.58	29.63	1.56	0.39	24.81
SR	573	10	20	None	53.08	5.49	5.04	36.39	0.82	0.49	19.31
	573	10	20	NaOH	54.45	5.62	4.57	35.36	0.95	0.51	20.15
Feed	–	–	–	–	43.06	6.08	4.26	46.60	1.42	0.81	14.93

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

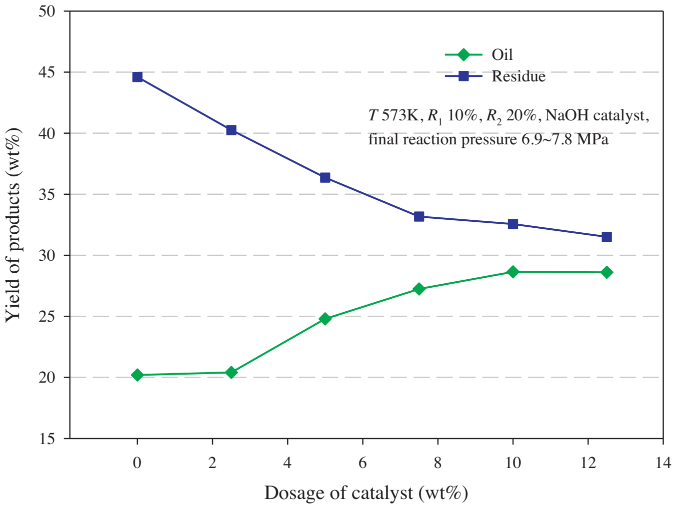

Fig. 6. Yields of bio-oil and SR varied with the dosage of catalyst (R_3).

catalyst (i.e., 5%). It is of interest to evaluate the catalytic activity of the catalysts at various dosages. For this end, NaOH (the best catalyst identified in Fig. 5) was tested at various dosages ranging from 0 to 12.5% and the results are presented in Fig. 6. As clearly shown in Fig. 6, the effect of NaOH on bio-oil and SR yields was strongly dependent on the dosage of catalyst. An increasing NaOH load corresponded to a decrease in SR yield (from 44.6% without NaOH to 31.5% with 12.5% NaOH), indicating an enhanced biomass conversion efficiency. For catalyst dosages lower than 2.5%, there was no obvious promoting effect to the bio-oil production. When the dosage of NaOH exceeded 2.5%, the yield of bio-oil continuously increased and leveled off at catalyst dosages higher than 7.5%. The possible reason may be that the catalyst not only promotes depolymerization but also re-polymerization. The latter process may dominate the former at high catalyst concentrations (dosages) [22].

3.5. Properties of the solid and liquid products

In addition to the liquefaction yields as discussed above, the properties of solid and liquid products resulting from the liquefaction operations were also of interest in this work.

3.5.1. Elemental analyses

The elemental compositions and other properties of bio-oil and SR obtained under different conditions are summarized in Table 2. Compared with the elemental composition of the crude rice husk, the obtained bio-oils had higher contents of carbon and hydrogen but lower concentrations of oxygen, leading to increased caloric values. As shown in the table, the HHVs of bio-oils were both higher than 20 MJ/kg, while the HHVs of the crude rice husk was only 14.93 MJ/kg. Moreover, the O/C atomic ratio of bio-oils decreased and the H/C atomic ratio increased. The significant reduction of oxygen content in bio-oils was mainly due to the dehydration reactions and the formation of CO/CO_2 in the liquefaction process [14]. In addition, the nitrogen content of bio-oils was higher than that of the raw material.

The content of oxygen in fossil oil ranged from 0.05% to 1.5%. As respect to nitrogen, the concentration distributed between 0.01% and 0.7% [20]. Compared to fossil oil, the oxygen and nitrogen contents in bio-oil were still too high to use this product oil as a gasoline or diesel fuel substitute. NO_x pollutants would form after the burning of bio-oil products, which was undesirable for environmental and legislative reasons. Thus, denitrogenation and additional deoxygenation are needed for an improved bio-fuel.

As revealed in Table 2, the addition of NaOH catalyst in the liquefaction process further increased the content of carbon and hydrogen in bio-oil but reduced the concentration of oxygen. The results quoted above may be accounted for by the enhanced hydro-cracking and hydrogenation reactions. In other words, the dehydration reactions were improved and the formation of CO/CO_2 was relatively weakened (by using NaOH as catalyst). Therefore, the bio-oil obtained with NaOH as catalyst had a higher caloric value compared with that produced without catalyst.

After liquefaction, the rice husk was converted into a carbonaceous residue referred to as hydrochar. As shown in Table 2, the elemental composition of SR changed significantly as a result of carbonization. Due to the dehydration and decarboxylation reactions, the solid mass decreased and energy densification occurred. The energy densification factor defined as $HHV_{SR}/HHV_{feedstock}$ reached up to about 1.3. This carbonized SR (hydrochar) has enormous potential for environmental- and energy-related applications such as an adsorbent for harmful pollutants, feedstock for carbon fuel cells, and a soil amendment (similar to char from pyrolysis/gasification) [29].

3.5.2. GC–MS analysis

The bio-oils collected after the liquefaction of rice husk contained a complex mixture of hydrocarbons and have been analyzed by GC/MS. The identification of the main compounds was performed using a NIST mass spectral database. Table 3 gives a comparison of the identified compounds in the bio-oils from the liquefaction of rice husk at 573 K, R_1 10%, and R_2 20% with or without catalyst (NaOH). The total ion chromatograms of bio-oils are presented in Fig. 7. The peak area (%) for each compound identified was defined by percentage of the compound's chromatographic area out of the total area. Only those compounds with peak area (%) higher than 1% were presented in this table. The percentage values (by integration from total ion chromatogram) indicate the proportions of individual compounds in the bio-oil but do not present the actual concentration.

It is clearly seen that phenolic compounds (18%) are the major compounds identified in the bio-oil obtained from the liquefaction of rice husk without catalyst, followed by esters (15%), long-chain alkanes (11%), benzene ramifications (3.2%) and furan derivatives

Table 3
Major chemical compositions of bio-oils.

No.	RT (min)	Name of compound	Peak area (%)	
			No catalyst	NaOH
1	6.73	2-Furanmethanol ($C_5H_6O_2$)	1.1	–[a]
2	8.44	Phenol (C_6H_6O)	1.1	1.0
3	8.70	Decane ($C_{10}H_{22}$)	–	1.6
4	9.13	1,2-Cyclopentanedione, 3-methyl-($C_6H_8O_2$)	1.1	–
5	9.58	Pentanoic acid, 4-oxo-, ethyl ester ($C_7H_{12}O_3$)	1.5	–
6	9.77	Phenol, 4-methyl-(C_7H_8O)	1.1	–
7	9.86	Furan, 2-butyltetrahydro-($C_8H_{16}O$)	2.7	–
8	10.05	Phenol, 2-methoxy-($C_7H_8O_2$)	2.9	1.8
9	10.13	Undecane ($C_{11}H_{24}$)	1.9	2.9
10	10.79	3a,6-Methano-3aH-indene, 2,3,6,7-tetrahydro-($C_{10}H_{12}$)	–	1.3
11	10.95	Benzene, (1-methyl-1-propenyl)-, (E)-($C_{10}H_{12}$)	1.7	1.6
12	11.03	Phenol, 4-ethyl-($C_8H_{10}O$)	2.7	1.7
13	11.10	Phenol, 3-ethyl-($C_8H_{10}O$)	2.7	2.3
14	11.26	Butanedioic acid, diethyl ester ($C_8H_{14}O_4$)	1.0	–
15	11.48	Dodecane ($C_{12}H_{26}$)	3.8	3.2
16	11.52	Phenol, 3-ethoxy-($C_8H_{10}O_2$)	3.3	-
17	11.53	Tridecane ($C_{13}H_{28}$)	1.0	2.7
18	11.66	Undecane, 2,5-dimethyl-($C_{13}H_{28}$)	–	1.1
19	11.84	Naphthalene, 1,2,3,4-tetrahydro-2-methyl-($C_{11}H_{14}$)	–	1.0
20	12.09	Phenol, 2-ethyl-5-methyl-($C_9H_{12}O$)	–	1.4
21	12.34	2-(1-Hydroxyisoamyl)-1-methoxybenzene ($C_{12}H_{18}O_2$)	–	1.2
22	12.47	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-($C_{11}H_{14}$)	–	2.2
23	12.49	Pentanedioic acid, diethyl ester ($C_9H_{16}O_4$)	1.3	–
24	12.58	Phenol, 4-ethyl-2-methoxy-($C_9H_{12}O_2$)	2. 8	1.5
25	12.63	1,3-Dioxolane, 2-methyl-2- (4-methyl-3-cyclohexen-1-yl)- ($C_{11}H_{18}O_2$)	1.1	–
26	12.67	Benzene, 1,4-dimethoxy-2-methyl-($C_9H_{12}O_2$)	1.5	–
27	12.85	Pentadecane ($C_{15}H_{32}$)	2.6	2.4
28	12.93	3,4-Benzo-1,3,5-cycloheptatriene ($C_{11}H_{10}$)	–	2.0
29	13.19	Naphthalene, 2-methyl-($C_{11}H_{10}$)	–	1.6
30	13.46	Tridecane, 4-cyclohexyl-($C_{19}H_{38}$)	–	1.3
31	13.48	.beta.-D-Ribopyranoside, methyl ($C_6H_{12}O_5$)	2.2	–
32	13.67	Phenol, 2-methoxy-4-propyl-($C_{10}H_{14}O_2$)	1.2	–
33	13.69	Benzene, 1-butyl-4-methoxy-($C_{11}H_{16}O$)	–	1.9
34	13.78	(4-Hydroxy-3-methoxyphenyl)-2-ethanol ($C_9H_{12}O_3$)	2.0	–
35	13.90	.alpha.-d-Ribopyranoside, methyl ($C_6H_{12}O_5$)	1.0	–
36	13.96	Eicosane ($C_{20}H_{42}$)	–	1.4
37	14.05	Tetradecane ($C_{14}H_{30}$)	1.7	4.5
38	14.06	Heptadecane ($C_{17}H_{36}$)	–	4.0
39	14.20	Naphthalene, 1,2-dimethyl-($C_{12}H_{12}$)	–	1.3
40	14.59	2-Pyrrolidinecarboxylic acid-5-oxo-, ethyl ester ($C_7H_{11}NO_3$)	1.1	–
41	14.68	Dimethyl phthalate ($C_{10}H_{10}O_4$)	–	1.6
42	14.76	2,5-Dimethyl-para-anisaldehyde ($C_{10}H_{12}O_2$)	–	1.1
43	14.80	Benzoic acid, 2-(1-oxopropyl)-, methyl ester ($C_{11}H_{12}O_3$)	–	1.2
44	15.10	.beta.-D-Glucopyranose, 1,6-anhydro-($C_6H_{10}O_5$)	3.5	
45	15.21	Nonadecane ($C_{19}H_{40}$)	–	2.7
46	16.35	Octadecane ($C_{18}H_{38}$)	–	1.7
47	16.60	Ethyl .alpha.-d-glucopyranoside ($C_8H_{16}O_6$)	1.7	–
48	17.08	Benzenepropanoic acid, 4-hydroxy-, methyl ester ($C_{10}H_{12}O_3$)	1.3	–
49	19.90	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester ($C_{16}H_{22}O_4$)	1.0	1.2
50	20.93	Phthalic acid, butyl undecyl ester ($C_{23}H_{36}O_4$)	1.2	–
51	21.10	Dibutyl phthalate ($C_{16}H_{22}O_4$)	4.1	4.5
52	21.37	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	1.3	–
53	23.5	Ethyl oleate ($C_{20}H_{38}O_2$)	1.4	–
Total			61	63

[a] Not detected or peak area less than 1% of total area.

(2.7%). In the case of using NaOH as catalyst, the main components of bio-oil are long-chain alkanes (30%); and the contents of phenolic compounds (9.7%), esters (8.5%) and naphthalene derivatives (7.1%) were the next. A conclusion may be made that the formation of alkanes was enhanced by the NaOH catalyst, e.g., the relative concentration of long-chain alkanes in the bio-oil was 11% without catalyst, while it increased dramatically to 30% in the presence of NaOH.

Compared with the results reported by Karagöz et al. [11] on liquefaction of rice husk at 553 K in water, the adoption of ethanol as solvent during the rice husk liquefaction resulted in not only higher yields of bio-oil but also different compositions of bio-oil. For instance, the liquid product obtained by Karagöz et al. [11] contained little amounts of esters (0.8% in acetone extract), while the bio-oils produced in this study had a much higher content of esters. As shown in Table 3, without catalyst the content of esters reached up to 15%. In the presence of NaOH catalyst, the concentration of esters was 11%. Meanwhile, no alkane was identified in the work of Karagöz et al. [11], but a significant amount of long-chain alkanes were detected in this study. In this case, it seemed feasible that the presence of ethanol could promote the formation of long-chain alkanes.

The phenolic compounds were primarily originated from the degradation of the lignin component in risk husk (by cleavage of the aryl ether linkages in lignin). The furan derivatives and the acids were formed primarily from the cellulose and hemicellulose components of rice husk [21]. A large quantity of esters were obtained from the liquefaction of rice husk with ethanol as

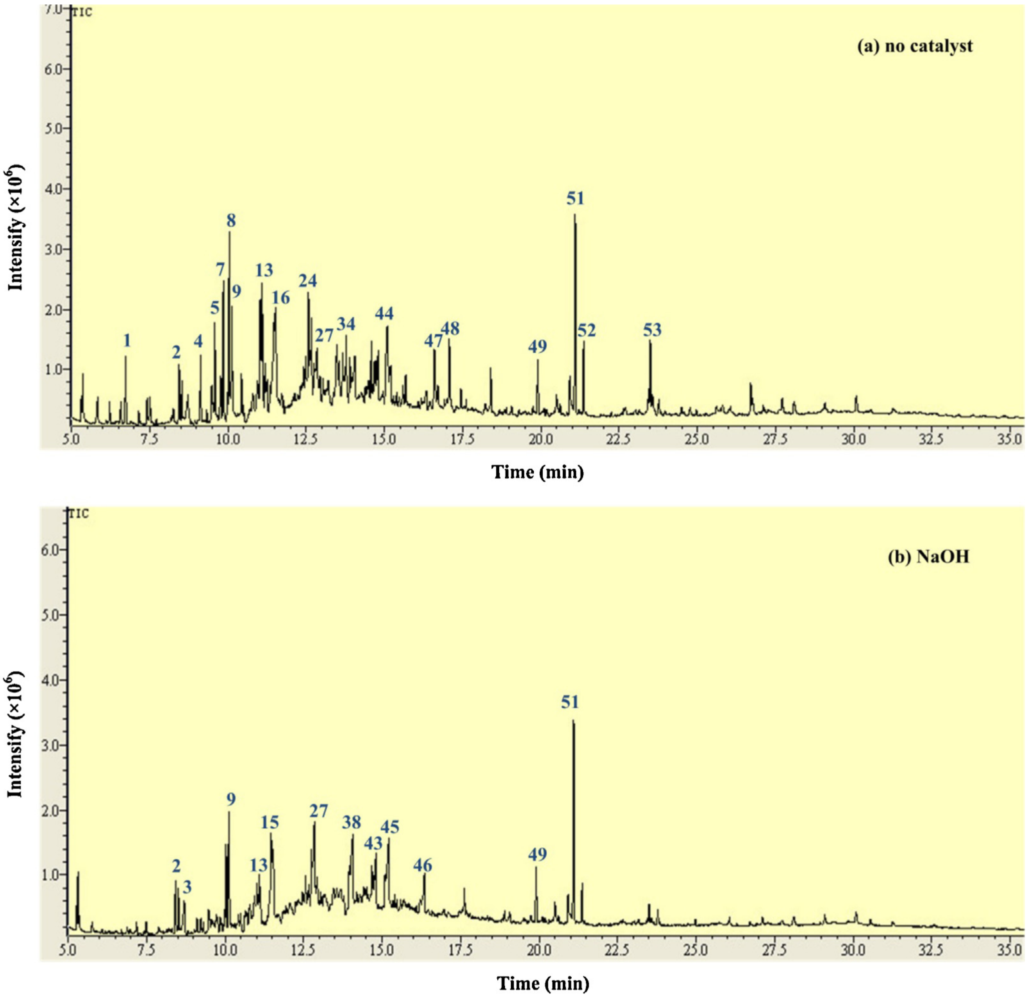

Fig. 7. Total ion chromatograms of bio-oils.

solvent, which may be ascribed to the esterification reactions between fatty acid and ethanol [14]. Fatty acid can also be partly degraded through decarboxylation at hydrothermal conditions to produce long-chained hydrocarbons [30].

The stability of the anionic form of carboxylic acid is lower than that of the non-anionic form [31]. The decarboxylation of the anionic form is faster than that of the molecular form. The addition of alkali hydroxide can promote the dissociation of R-COOH into R-COO$^-$ and H$^+$ [32]. In the current study, the addition of NaOH increased the yield of alkanes but reduced the ester yield. One rational explanation may be that the addition of NaOH enhanced the dissociation of fatty acid into anionic form. Then the decarboxylation of fatty acid, producing alkanes, was improved and the esterification reactions between fatty acid and ethanol, forming esters, were relatively weakened. Watanabe et al. studied the decomposition of stearic acid ($C_{17}H_{35}COOH$) under supercritical conditions and found that the addition of NaOH could accelerate the decomposition process, and higher yields of alkanes were obtained [33].

4. Conclusions

Higher feedstock/solvent ratios resulted in lower yields of bio-oil. With increasing reaction temperature and solvent filling ratio, the bio-oil yields increased firstly and then decreased. In comparison with other tested catalysts (Na_2CO_3, FeS and $FeSO_4$), NaOH was verified as an ideal catalyst for liquefaction of rick husk in ethanol. The rational dosage of NaOH was about 10%. The solid products were carbonized to a certain extent. The bio-oils were mainly constituted of phenolic compounds, long-chain alkanes and esters. Adopting ethanol as the liquefaction solvent appeared to promote the formation of long-chain alkanes and esters. In addition, the alkane formation was further enhanced by the NaOH catalyst.

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