

Subcritical and Supercritical Water Liquefaction of Rice Husk for Production of Heavy Oil and SiO₂ Gel

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ABSTRACT

Liquefaction of rice husk in sub/supercritical water was investigated with and without Na₂CO₃ catalyst. Experiments were conducted in a 150 ml high-pressure autoclave reactor at temperatures ranging of 280-380 °C for 10-90 min. The influence of temperature, reaction time and mass ratio of rice-to-water on products distribution was discussed in present work. The optimization of experimental operations was confirmed at 300 °C for 10 min with the R/W ratio of 0.2. The maximum of heavy oil yield was found to be 29.8 wt%, which was obtained under optimum operations with 12 wt% Na₂CO₃. The heavy oils from with and without catalyst were identified using FTIR and GC-MS. The results showed that the heavy oil from without catalyst mainly contained phenolic compounds, ketones and carboxyl acids, while that from with Na₂CO₃ mainly consisted of phenol derivatives, esters, long-chain hydrocarbons, ketones and alcohols. Silicon dioxide gel was obtained by treatments of solid residue from subcritical water liquefaction of rice husk. The particle size of silica gel was found to be in the range of 50-100nm by means of SEM.

KEYWORDS:

Biomass, sub/supercritical water, liquefaction, heavy oil

1. INTRODUCTION

Nowadays, alternative and renewable energies have received great attention due to the global warming, the increased demand for energy and energy security^[1]. Biomass is the only practical source to generate liquid fuel utilized in the prevailing automotive infrastructure among all renewable sources. Biomass resources can be categorized into agricultural residue such as forestry waste and crops waste, municipal solid waste, animal manure, waste water and black liquor etc^[2, 3]. Rice husk is one of important agricultural residues, and its output reaches approximately 54 million tons every year in China^[4]. A significant proportion of rice husk suffers direct combustion in some rural areas, which causes serious environmental issues. Rice husk consists of not only cellulose, hemi-cellulose, lignin and extractives but also about 15-20 % SiO₂ as a potential feature^[5, 6]. Hence, rice husk is considered as important carbon and silicon resource for producing biofuel and silica materials.

The methods for conversion biomass to fuel include biochemical processes (fermentation) and thermochemical processes (gasification, pyrolysis, liquefaction and hydrolysis). Biochemical process can decompose biomass to bio-methanol and bio-ethanol in a mild

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condition, but long reaction period is a drawback. Gasification and pyrolysis technologies have also its own advantages, but they usually have a requirement for low water content and small particle size. Compared to these approaches, liquefaction technology especially utilizing water as solvent can be performed to convert wet biomass to fuel.

Sub/supercritical water is attracting more and more attention as a green reaction medium for its environmentally benign property. Sub/supercritical water become a promising solvent in the processes of biomass liquefaction^[7] as they possess of the distinctive properties, such as low dielectric constant and viscosity, enhanced dissociation constant (K_w), weak hydrogen bonds,. H. Mazaheri et al.^[8] found that oil palm fruit press fiber was decomposed to various liquid products in subcritical water with and without catalyst. P. Duan et al.^[9] reported hydrothermal liquefaction of microalgae with heterogeneous catalysts at 350 °C under inert and high-pressure reducing conditions. C. Xu et al.^[10] obtained heavy oils with high caloric values by direct liquefaction of woody biomass in subcritical water with and without catalyst at 280-380 °C. Direct liquefaction of paulownia in hot compressed water were conducted at 280-360 °C for 10 min with Na_2CO_3 and Fe catalyst. The effects of temperature and catalyst on yield of heavy oil were discussed, and then the composition of heavy oils was identified by GC-MS. The results showed that the heavy oil mainly contained phenol derivatives, ketones, carboxylic acid, benzene derivatives and long-chain alkanes^[11, 12].

The hydrothermal processing of rice husk was investigated in previous reports. R. Vegas et al.^[13] found that auto-hydrolysis of rice husk was occurred at low temperature (180 °C) for 15-40 min. C. Wang et al.^[14] carried out the deoxy-liquefaction of four different biomass sample (including rice husk) at 350 °C in the desired proportions between biomass and water for 2-3 h. However, a systematic experimental study on sub/supercritical water liquefaction of rice husk in a wide range of operational conditions (temperatures, reaction time, the ratio of rice to water) with and without catalyst had not been executed so far.

The objectives of this work is to investigate the effects of temperatures, reaction time, ratio of rice to water and Na_2CO_3 catalyst on the yields of liquid and solid products. The composition of heavy oils was assessed by FTTR and GC-MS. The silica gel derived from solid residue was also observed by SEM.

2. MATERIALS AND METHODS

The rice husk was taken from Jiangsu province in China. The air-dried rice husk was grinded and screened. Only the fractions that size smaller than 4 mm were selected in this work. Liquefaction experiments were conducted in a 150 ml autoclave at reaction temperatures. Water in the presence/absence of sodium carbonate was used in the experiments. In each run, the reactor was heated from ambient temperature to the desired temperature.

Experiments were performed at varying temperatures between 280 and 380 °C. The optimal reaction time and the optimal mass ratio of rice husk to the de-ionized water were obtained at 300 °C. In a typical run, 10 g of air-dried rice husk was weighted into the reactor, followed by the addition of catalyst (if needed) in an amount of the mass ratio from 4 wt% to 14 wt% of the rice husk, and then, 50ml de-ionized water was added. Reactor was sealed and then was vacuumized. With heating rate of 10 °C/min, reactions proceeded at specified temperature ranging from 280 to 360°C for a desired residence time (varying from 10 min up to 90 min). Subsequently, Heating was stopped and the autoclave temperature was dropped to room temperature by air fan.

After each run, the gas was vented. The gas products were not analyzed in this work, because our main interest is in the liquid and solid products. The liquid and solid products were removed from the autoclave into a beaker, the reactor was rinsed repeatedly by de-ionized water and rinsing water was collected. The mixed products were filtered under vacuum to separate the water insoluble fraction. The filtered water phase was evaporated at 50 °C under reduced pressure in a rotary evaporator to obtain the water soluble residue. After that, the autoclave was washed by 100 ml of acetone, and then the acetone soluble fraction was poured in a beaker in which the water insoluble fraction was collected in advance. The acetone soluble fraction was also filtered to separate the acetone insoluble fraction. The acetone solution was dried at 30 °C in a rotary evaporator, and then got the acetone soluble residue. The acetone insoluble fraction was then dried until constant weight in an oven at 105 °C. These products were the so-called water soluble oil (WSO), heavy oil (HO, acetone soluble residue) or tar and solid residues (SR, acetone insoluble fraction), respectively^[11]. In the presence of sodium carbonate runs, we supposed all the catalyst was retained in the solid residues, so the solid residues yields were revised by excluding the catalyst amount.

Silicon dioxide, the predominant compound in the solid residues, was extracted via four steps. The solid residue ash was obtained by calcination at 550 °C in a tube furnace for 4 hours. The weighted residue ash was loaded into a round bottom flask, and then hydrochloric acid (3 mol·L⁻¹) was added to remove metal impurities. The sample was continuously agitated and heated until boiling, cooled to ambient temperature. After filtering, the ash was treated with sodium hydroxide (1 mol·L⁻¹) to dissolve the silicon dioxide present in the sample, thus producing sodium silicate. The gelification of sodium dioxide was formed by dropwise adding hydrochloric acid (3 mol·L⁻¹) into sodium silicate solution to neutral. To purify gel, the washing process was requisite to removed sodium chloride by using de-ionized water and ethyl alcohol. Finally, the formation of silicon dioxide was obtained by drying the humid gel

at 160 °C in the oven.

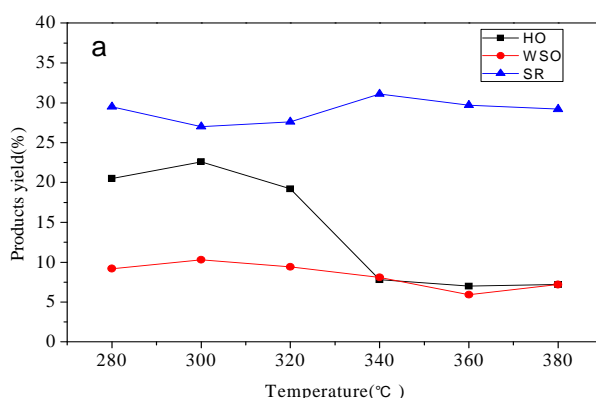
The composition of HO and WSO were identified by a Gas Chromatograph Mass Spectrometer (GC-MS) respectively [Perkin Elmer Auto System XL GC/Turbo Mass MS; GC equipped with DB-5MS (30 m×0.25 mm×0.25µm); temperature program 60 °C (hold 4 min) to 290 °C (5 °C/min); carrier gas 99.999% He; Ionization mode EI; Mass scan range 33-550 m/z]. Compounds in the HOs were identified by means of the NIST 98 and WILEY7.0 MS library. The FTIR spectra of the HO were recorded using a Perkin Elmer Spectrum 100 within the range of 4000-400 cm⁻¹ by the KBr tablet technique.

3. RESULTS

3.1 Liquefaction of rice husk in pure sub/supercritical water

3.1.1 Effects of Reaction Temperature

The effects of reaction temperature on the products yields can be revealed from the Fig. 1(a). The data in this figure were obtained from the liquefaction of rice husk at the reaction conditions of various temperatures ranging from 280 °C to 380 °C without catalyst, the mass ratio of 0.2 (rice husk / water) and the time of 10 min. At all temperatures in the range of 280-360 °C, generally, the yields of the HO (7.0-22.6 wt%) were much greater than that of the WSO (5.9-10.3 wt%). Similar liquid products (HO and WSO) yield was reported in many other studies ^[15, 16], the slight difference can be attribute to the variety of biomass. As can be clearly shown that the yields of HO and WSO increased with the increasing temperature up to 300 °C, and they decreased drastically with temperature increasing further.



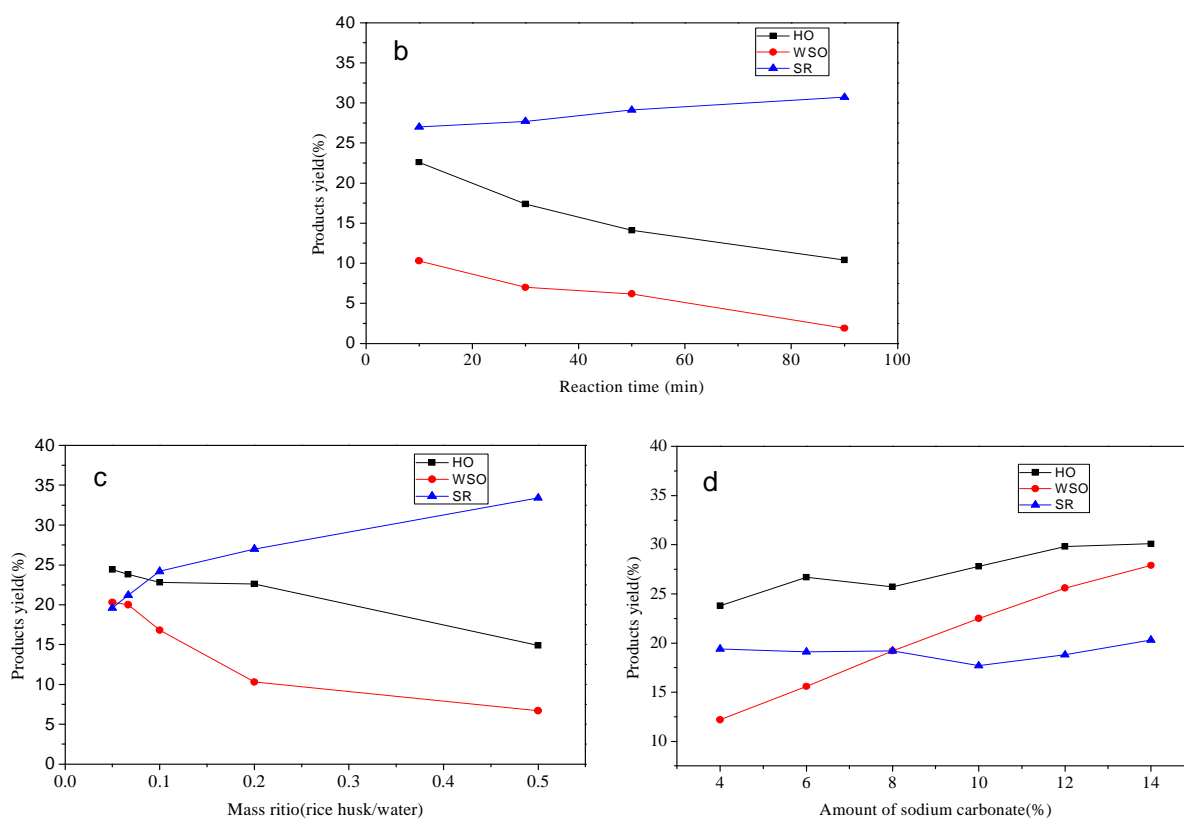


Figure 1. Effects of operation conditions on products yield in sub/supercritical water liquefaction of the rice husk with and without catalyst. (a) reaction temperature; (b) reaction time; (c) mass ratio of rice-to-water; (d) Na_2CO_3 ranging from 4 wt% to 14 wt% at 300 °C for 10 min with rice-to-water ratio of 0.2.

3.1.2 Effects of Reaction Time

Fig. 1(b) shows the yields of the HO, WSO and SR in liquefaction of rice husk at the conditions of temperature of 300 °C without catalyst and the rice-to-water ratio of 0.2. Clearly shown in Fig. 1(b), the yield of the HO and WSO decreased monotonously as prolonging reaction time, while that of the SR increased with the time in the range from 10 min to 90 min. The results presented that longer reaction led to negative formation of the HO and WSO. Similar results can be observed from the previous work about the biomass liquefaction in sub/supercritical water or hydrothermal process [17,18]. In the initial stage, rice husk was hydrolyzed to many heavy intermediates that were active in subcritical water. The heavy intermediates can be converted into liquids, gases and solid residues in the secondary and tertiary reactions. However, liquid products also can be degraded into lighter molecules or coked into bio-char for longer residence time, which promoted the formation of the gases and solid residues.

3.1.3 Effects of Rice-to-Water Ratio

Rice husk were subjected to subcritical water liquefaction at the conditions of the temperature of 300 °C without catalyst, the time of 10 min and the mass ratio of rice to water (R/W) ranging from 0.05 to 0.5. Fig. 1(c) shows the conversion of rice husk to liquids (HO

and WSO) and solid residue. It was clearly shown that a lower R/W ratio produced higher yields of liquid product and lower solid residue. As noted previously (3.1.2), heavy intermediates were initially produced in liquefaction of rice husk, and then they were interacted with themselves or water solvent to produce SR, or liquids and gases in the secondary reactions. A higher heavy intermediates concentration obtained with a higher R/W ratio offered more opportunity of interaction with themselves to generate SR. H. Li et al. and D. Knezevic et al.^[19,20] also described that a higher R/W ratio might prohibit the solvolysis/hydrolysis of the lignocellulosic solids, resulting in a lower yields of HO and a higher yields of char.

However, it is true that a low R/W ratio costs considerable heating energy. Thus, a rice husk to water ratio of 0.2 was suitable in view of relatively higher yield of HO and lower energy consumption.

3.2 Effects of Sodium Carbonate Catalyst

The rice husk liquefaction were conducted under the conditions of the temperature of 300 °C, the time of 10 min and 0.2 R/W ratio with Na₂CO₃ catalyst. Fig. 1(d) shows the effects of concentration of Na₂CO₃ catalyst on the yields of liquid and solid products. Na₂CO₃ catalyst increased the yields of HO, WSO, and inhibited the formation of char. The yield of HO was found in the range of 23.8-29.8 wt% with the Na₂CO₃ concentration less than 12 wt%, while the yield of HO improved inconspicuously when concentration of catalyst increased further. The optimum yield of HO (29.8 wt %) was obtained in the presence of 12 wt% Na₂CO₃. The yield of WSO varied tremendously from 12.2 wt% to 27.9 wt%. In addition, compared with the results without catalyst, the yield of SR dropped to between 18.7 wt% and 21.7 wt% from around 27 wt%. This might be due to Na₂CO₃ preventing the dehydration and promoting the hydrolysis / cracking reaction by oxygen transfer mechanism^[18, 21].

3.3 Characterizations of the Liquid and solid products

3.3.1 FTIR analysis of heavy oils

Fig. 2 shows the FT-IR spectrum of heavy oils obtained at the conditions of 300 °C, 10 min and with R/W ratio of 0.2 with and without 12 wt % Na₂CO₃ catalyst. The bands and absorption intensity of heavy oils had great change when the Na₂CO₃ catalyst was added.

As shown in the fig. 2(a), without Na₂CO₃ catalyst, a broad and strong absorption peak at 3200-3600 cm⁻¹ suggested the stretching vibration of O-H group, and the maximum absorption peak drifted from 3396 cm⁻¹ to 3369 cm⁻¹ revealed the presence of phenolic compounds and carboxylic acids. C-H group stretching vibration had a strong and narrow absorption at 2926 cm⁻¹. The weak peaks from 2371 cm⁻¹ to 2297 cm⁻¹ which had no overlap with bands from HO, were caused by carbon dioxide in sample cell. The low-intensity absorption at 1969 cm⁻¹ were the character of C=O in ketones and carboxyl acids. The peaks at 1608 cm⁻¹, 1515 cm⁻¹ and 1457 cm⁻¹ represented C=C group stretching vibration in aromatic skeletal, which

indicated there could be aromatic compounds or their derivatives. The peaks at 1384 cm^{-1} and 1261 cm^{-1} represented the C-H group bending vibration and C-O group stretching vibration, which suggested the presence of syringyl ring^[12]. Hence, the HO (a) may be composed with aromatic and its derivatives, ketones and carboxyl acids.

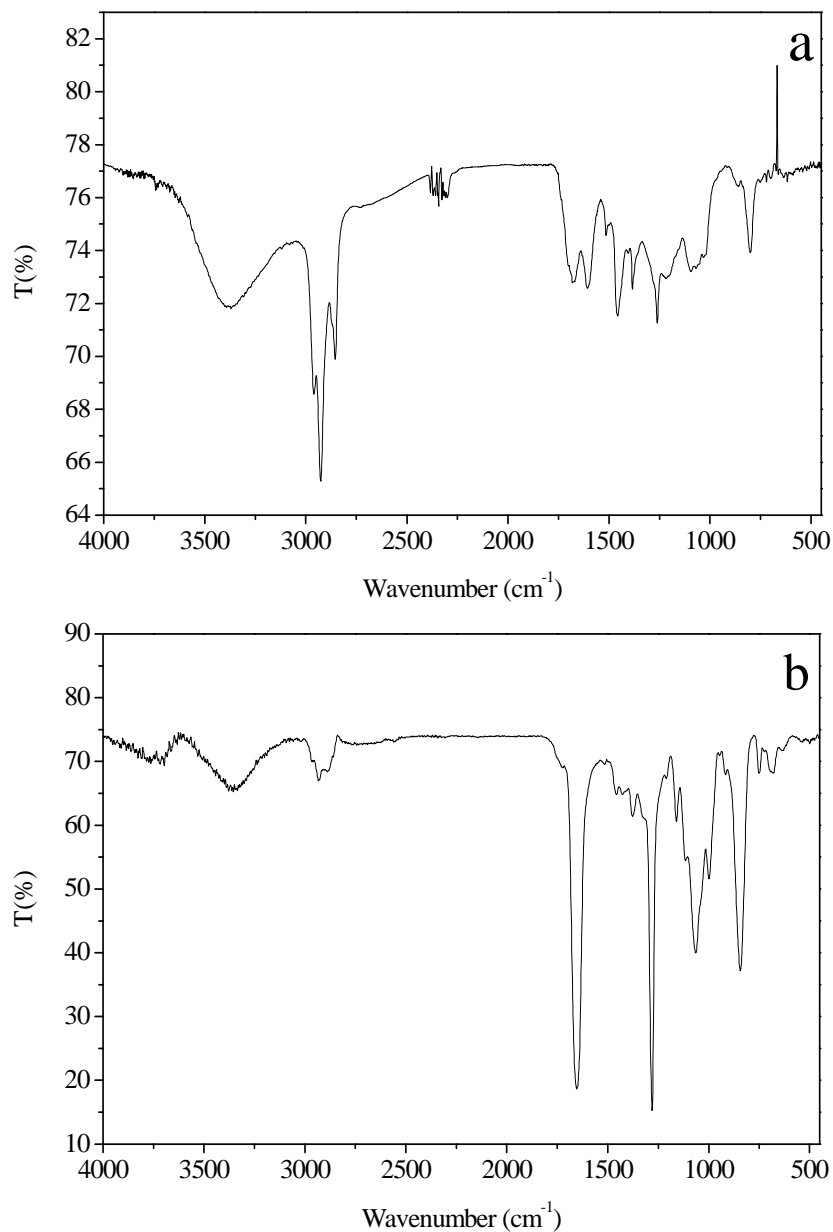


Figure 2. FT-IR spectrum of heavy oils with and without catalyst. (a) without catalyst; (b) with 12 wt % Na_2CO_3 .

However, as seen from fig. 2(b), with 12 wt% Na_2CO_3 catalyst, a novel peak at 3697 cm^{-1} emerged and might be attributed to O-H group stretching vibration from alcohols. The lower intensity of peak at $3200\text{-}3600\text{ cm}^{-1}$ than that of fig. 2(a) suggested the decreased concentration of phenolhydroxyl. The bands representing C-H group stretching in aliphatic compounds appeared in the $2800\text{-}3000\text{ cm}^{-1}$ range whether Na_2CO_3 catalyst was present or not. Interestingly, another novel peak with strong absorption appeared at 1654 cm^{-1} , which could be resulted from C=C group stretching vibration in alkenes. The peak at 1377 cm^{-1} was

accused by methyl symmetrical C-H bending vibration. Besides, two strong and sharp peaks at 1280 cm^{-1} , 1064 cm^{-1} were the response to C-O-C stretching vibration from aliphatic esters. Consequently, the differences of HO component were clearly existent between with catalyst and without catalyst in the liquefaction of rice husk. The HO (b) may be consisted of phenolic compounds and their derivatives, hydrocarbons, esters and ketones etc.

3.3.2 Composition of heavy oils

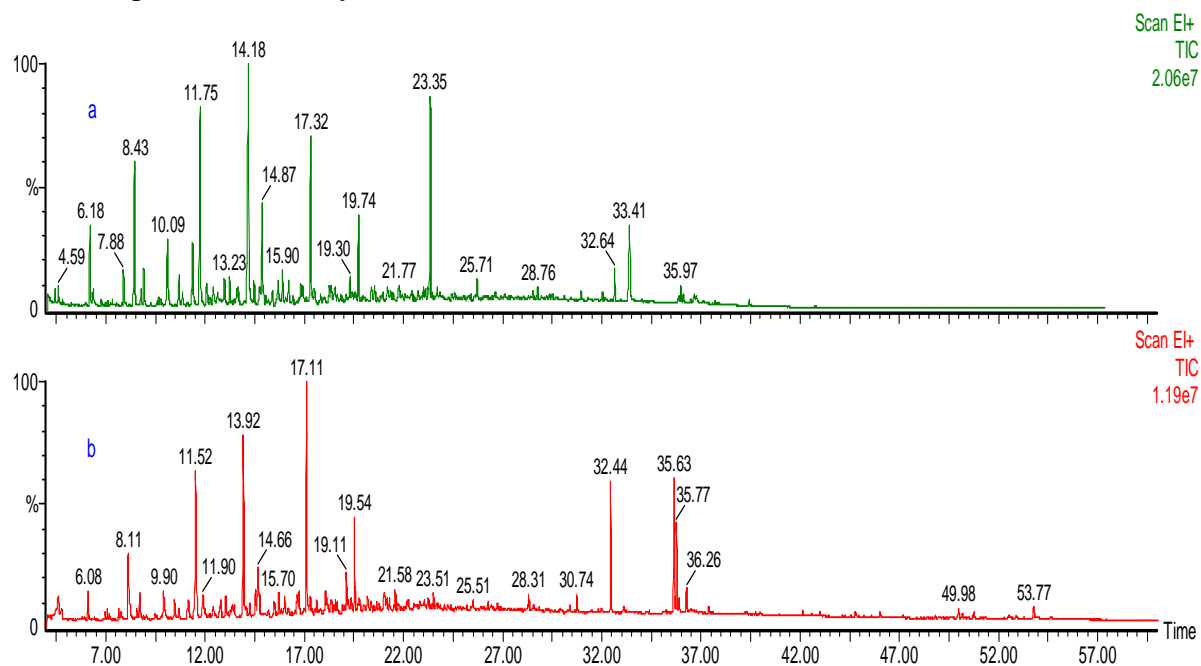


Figure 3. Total ion chromatogram of the HOs from the liquefaction of rice husk at $300\text{ }^{\circ}\text{C}$ for 10 min with R/W of 0.2 with and without Na_2CO_3 catalyst. (a) without catalyst; (b) with 12 wt % Na_2CO_3 .

The compositions of the heavy oils obtained with and without Na_2CO_3 catalyst at temperature of $300\text{ }^{\circ}\text{C}$ were qualitatively characterized by GC-MS. Fig. 3 shows TIC of the

HOs from the liquefaction of rice husk at $300\text{ }^{\circ}\text{C}$ for 10 min with R/W of 0.2 with and without Na_2CO_3 catalyst. The GC-MS analysis results for HO (with catalyst) was also listed in table 1, that showed the area percentage content for the main compounds identified (defined by the percentage of the compound's chromatographic area out of the total area). It was obviously shown in table 1, that HOs mainly consisted of phenolic compounds and derivatives irrespective of whether catalyst was present or not. For HO obtained with Na_2CO_3 , phenolic compounds and derivatives accounted for about 35.95 % of the total peak area, followed by esters (11.34 %), long-chain hydrocarbons (8.12 %), ketones (7.89 %) and alcohols (3.91 %). The HO mainly contained 2-methoxyphenol, 4-ethyl-2-methoxyphenol, hexen-1-ylcyclonexane, 2-hydroxy-2-cyclopenten-1-one, 9,12-octadecadienoic-methylester, phenol, 2-(2-propynyloxy)-ethanol, 4-ethylphenol, etc. However, for HO obtained without catalyst, phenolic compounds and derivatives accounted for about 58 % of the total peak area, followed by cyclopenten ketones(9.24 %) and carboxylic acids(5.68 %). The compounds in HO mainly contained 3-ethylphenol, mequinol, butylated hydroxytoluene,

4-ethyl-2-methoxyphenol, 4-methylphenol, 2-methoxy-4-methylphenol, n-hexadecanoic acid, phenol, 2-methoxy-4-propylphenol, 2,3-dimethyl-2-cyclopenten-1-one etc. Na_2CO_3 catalyst altered the composition of HO, and inhibited the formation of carboxylic acids due to neutralization reaction between with themselves. The carboxylic acids may be primarily originated from hydrolysis and dehydration of rice husk extractives^[22], while phenolic compounds may be primarily formed via degradation reaction of lignin in liquefaction process and condensation/cyclization of holocellulose-derived carbohydrates^[23].

Table 1. GC-MS analysis results for HO.

Peak no	RT/min	Compounds	Area %
1	4.178	3-methoxycarbonyl-3-methyl-1,2,4-trioxolane	1.70
2	4.597	2-cyclopenten-1-one,2-hydroxy-	4.64
3	4.768	ethanol, 2-(2-propynyloxy)	2.01
4	6.083	spiropentane	0.87
5	8.106	phenol	3.93
6	8.705	sprio[2.4]heptan-4-one	0.82
7	9.904	2-cyclopenten-1-one,2,3-dimethyl-	1.44
8	10.446	dl-erythro-1-phenyl-1,2-propanediol	0.92
9	11.143	phenol,3-methyl-	1.19
10	11.518	phenol,2-methoxy-	8.17
11	11.898	hexen-1-ylcyclonexane	1.59
12	12.776	1,3-hexadiene,3-ethyl-2-methyl-	1.12
13	13.028	phenol,2-ethyl-	0.84
14	13.916	phenol,4-ethyl-	7.34
15	14.54	1,8-dimethylspiro[4.5]decane	1.00
16	14.656	2-methoxy-6-methylphenol	1.65
17	15.478	1,3-hexadiene,3-ethyl-2,5-dimethyl-	0.89
18	15.696	cyclonexene,3-methyl-6-(1-methylethylidene)-	0.98
19	16.652	o-methoxy-alpha-methylbenzyl alcohol	0.98
20	16.72	cyclopenta[c]pyran-1,3-dione,4,4A,5,6-tetrahydro-4,7-dimethyl-	0.88
21	17.11	phenol,4-ethyl-2-methoxy-	7.74
22	17.304	1H-inden-1-one,2,3-dihydro-	0.92
23	18.059	phenol,3,5-diethyl-	0.98
24	19.11	phenol,2,6-dimethoxy-	1.38
25	19.536	phenol,2-methoxy-4-propyl-	2.73
26	21.009	3,4-dihydroxymethylmethylphene,2-methyl-	1.03
27	21.58	1,3-cyclohexadiene,5-butyl-	0.86
28	32.445	hexadecanoic acid,methyl ester	3.88
29	35.635	9,12-octadecadienoic,methyl ester	3.93
30	35.766	10-octadecenoic acid,methyl ester	2.65
31	36.258	tetradecanoic acid,12-methyl-,methyl ester,(s)-	0.88
Total area%			69.95

3.3.3 Preparation of Silica gel

Silicon dioxide gel originated from producing solid residue in subcritical water liquefaction of rice husk with 12 wt% Na_2CO_3 was obtained by a series of procedures, such as calcination, acid leaching, aging and gelification. The yield of silicon dioxide (based on dry rice husk liquefaction ash) reached up to 71.4 wt%, which was higher than that of previous reports [24]. The morphology analysis of silicon dioxide gel particles was performed with scanning electron microscopy (SEM). It was clearly shown in fig. 4, that particle size of the

silicon dioxide gel was distributed equably in the range of 50-100nm. The amorphous product with small particle size can be of use as catalyst support^[25], thixotropic agents, thermal insulators, composite fillers, etc. ^[24].

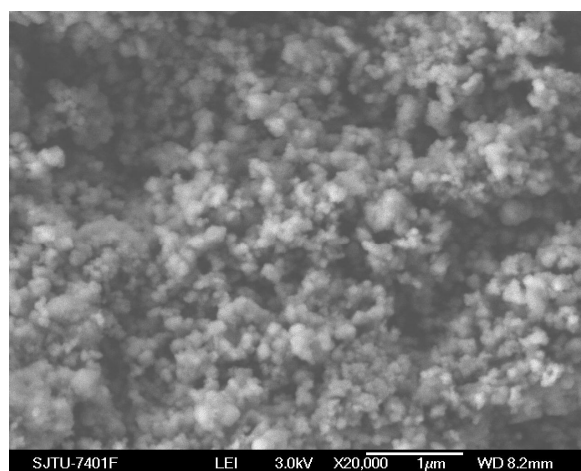


Fig. 4 SEM image of SiO₂ gel

4. CONCLUSION

The efficient decomposition of rice husk was performed by direct liquefaction in sub/supercritical water with and without Na₂CO₃ catalyst. The experimental results showed that the yields of HO and WSO initially increased with increasing temperature up to 300 °C, and then it decreased drastically with temperature increasing further. The yields of HO and WSO generally declined with reaction time prolonged and increasing the ratio of rice-to-water. The optimization of experimental operations was confirmed at 300 °C for 10 min with the R/W ratio of 0.2. In this work, the maximum yield of HO was found to be 29.8 wt% in the presence of 12 wt% Na₂CO₃, corresponding the yield of solid residue dropped to 18.8 wt%. The HOs obtained with and without catalyst were analyzed using FTIR and GC-MS. The composition of HO was effected by adding Na₂CO₃ and characterized by phenolic compounds and derivatives, esters, long-chain hydrocarbons, ketones and alcohols. Silicon dioxide gel with 50-100nm range particle size was obtained by a series of procedures, such as calcination, acid leaching, aging and gelification.

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