

# The Effect of Different Catalysts and Process Parameters on the Chemical Content of Bio-oils from Hydrothermal Liquefaction of Sugarcane Bagasse

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The effects of temperature, reaction time, biomass/water feedstock ratio, NaOH concentration, and ZSM-5 catalyst amount were investigated relative to the hydrothermal liquefaction (HTL) of sugarcane bagasse. The experimental results showed that the maximum yield of bio-oil (46.9%) was achieved with the following conditions: 10 g of sugarcane bagasse, 200 mL of distilled water, 30 min, and 285 °C. It was seen that the products of oxygenation (phenols, acids, ketones, alkenes, and esters) were abundant in the bio-oil. With the addition of NaOH, the residue yield decreased remarkably, and the yield of organics dissolved increased. The yields of acids and furfurals in the bio-oil decreased with the presence of NaOH during HTL. Additionally, ZSM-5 effectively decreased the acidic compounds and improved the liquid properties during HTL. Sugarcane bagasse in HTL with catalysts significantly improved the quality of bio-oil with lower oxygen content and higher HHV. Moreover, the gaseous products H<sub>2</sub> and CH<sub>4</sub> were noticeably affected by the temperature, NaOH concentration, and ZSM-5 amount.

*Keywords:* Hydrothermal liquefaction; Sugarcane bagasse; Bio-oil; NaOH; ZSM-5

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## INTRODUCTION

With rapid industrialization and urbanization occurring around the world, there has been a major increase in the global energy demand. According to statistics, there is still an overwhelming reliance on coal, oil, natural gas, and other conventional energy sources to meet global energy consumption requirements, even though non-renewable fossil energy sources are soon to be depleted. Renewable energy has received a great deal of attention because of environmental considerations and the increasing demand for clean energy worldwide. Biomass has a rich source, low prices, renewable character, and lower nitrogen and sulfur contents. Because of its low pollution emissions, biomass is commonly recognized as an important renewable energy source, and a lot of research has been carried out to convert it into transportable, high energy density liquid fuels (Pexa *et al.* 2016; Zhang *et al.* 2016; Yamada *et al.* 2017).

Thermochemical conversion is a commonly used method to upgrade biomass. It can be further divided into gasification, pyrolysis (Alma *et al.* 2016), and direct liquefaction (Chan *et al.* 2014; Chen *et al.* 2015). In general, compared with pyrolysis, hydrothermal liquefaction (HTL) is a more promising technology for biomass in that it requires no dewatering of the feedstock, thereby avoiding the loss of enthalpy energy. Moreover, biomass feedstock can be utilized without any pretreatment at a comparatively

low temperature. Bio-oil has lower oxygen content, therefore it has higher energy content than pyrolysis-derived oils (Peterson *et al.* 2008). The process can convert biomass into small molecules in water, with or without a solvent and catalyst. These small molecules are not only unstable and reactive but can also repolymerize into oily compounds with a broad range of molecular weight distributions (Chen *et al.* 2012). The liquefaction of biomass has been investigated in the presence of alkaline solutions (Singh *et al.* 2015), alkali metal formates (Na *et al.* 2012; Yim *et al.* 2017), alcohols (Yan *et al.* 2010), hydrogen compounds from *in-situ* sources (Ramsurn and Gupta 2013), and glycerin (Pedersen *et al.* 2015, 2016). Numerous reviews of biomass resources and conversion processes have been published (Collard and Blin 2014; Hassan *et al.* 2016; Kabir and Hameed 2017). However, the usage of solvents in liquefaction likely increases the reaction pressure, due to their high volatility. In contrast, water is environmentally benign and inexpensive, and it has been widely used as a solvent for liquefaction (Qian *et al.* 2007).

China is an agricultural country with abundant biomass resources, including sugarcane bagasse. Sugarcane bagasse is a main byproduct of sugarcane syrup extraction and is an important renewable biomass resource with stable composition and uniform properties (Shaikh *et al.* 2009). However, due to backward technology, bagasse is often abandoned or utilized only for fuel; thereby its utilization is very low. As agricultural waste is abundantly available in China, researchers are interested in developing methods to convert it into oils and chemicals. It can be used in the production of high value-added products, which can meet the needs of continuity and uniformity requirements of industrialization. However, the bio-oil produced from biomass without catalyst cannot be used directly for transport, due to its high oxygen content which results in high acidity, high viscosity and high water content making it unstable (Lehto *et al.* 2014). Thence, there is need to upgraded bio-oil produced from sugarcane bagasse with catalyst.

Zeolite is a microporous crystalline material. It was recognized as a favorable catalyst used for biomass conversion with a tunable acidity, shape-selective microporous structure, and high surface area (Dusselier *et al.* 2015; Song *et al.* 2017). Addition of alkaline solutions in water is helped by enhancing the swelling of the cellulose, destroying the crystalline structure, increasing in surface area, and decreasing in the degree of polymerization (Fan *et al.* 1982). In this work, an experimental study was carried out in order to observe the HTL of sugarcane bagasse, a widely used agricultural byproduct grown in China, and the effects of the reaction temperature, time, biomass/water ratio on the oil yield. Meanwhile, different amounts of NaOH and ZSM-5 were added in order to improve the yield and quality of bio-oil.

## MATERIALS AND METHODS

### Materials

Sugarcane bagasse was obtained from local sources in Beijing, China. The sugarcane bagasse samples were ground to a 20-mesh size. The powder was then dried in an oven at 105 °C for 12 to 24 h and kept in a desiccator at room temperature (25 °C) until use. The typical composition of the sugarcane bagasse is as follow, cellulose (39.0%), hemicelluloses (24.9%), and lignin (23.1%) (Toor *et al.* 2011). The elemental composition of the sugarcane bagasse was analyzed with a Vario EL cube CHNSO elemental analyzer (Elementar, Frankfurt, Germany) (C: 44.7 wt.%, H: 5.3 wt.%, O: 47.6 wt.%, N: 0.4 wt.%). ZSM-5 zeolite (Si/Al = 38) from Tianjin Nan Hua catalyst co., LTD. (Tianjin, China) was

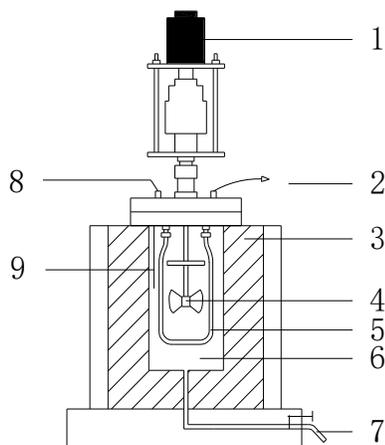
dried at 105 °C for 24 h before use. The properties of ZSM-5 are shown in Table 1. NaOH (Guaranteed reagent, Purity  $\geq$  98.0%) was purchased from Beijing Chemical Works, China.

**Table 1.** Textural Properties of ZSM-5

Sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Av pore diameter (nm)
ZSM-5	38	287.135	0.279	3.896

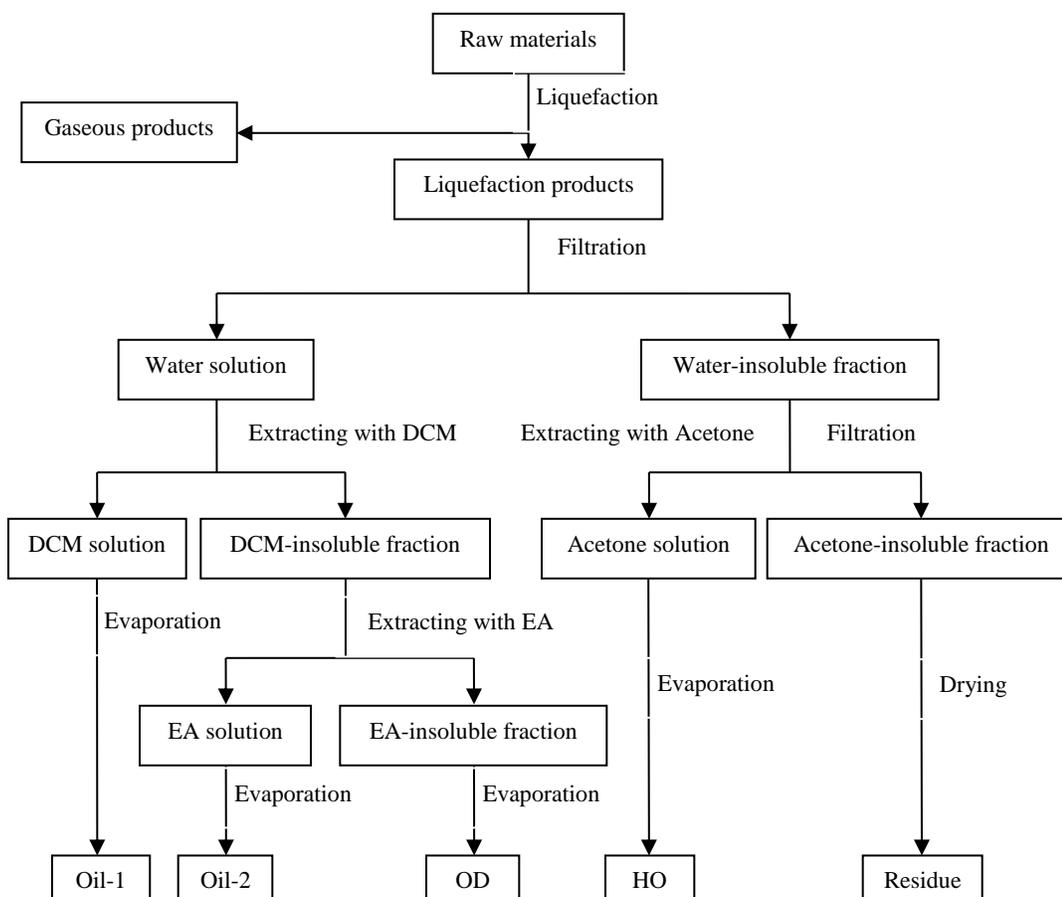
### Experimental Procedure

The HTL process was carried out in a 1-L stainless steel autoclave equipped with a stirrer, as shown in Fig. 1. The autoclave was heated with an external electrical furnace. A pre-determined amount of raw materials (*i.e.*, 3, 5, 8, 10, and 15 g) and 200 mL of distilled water were fed into the reactor. After the autoclave was sealed, it was heated to the reaction temperature (225, 255, 285, 315, and 345 °C) set point and the temperature was then kept constant for the desired reaction time (0, 15, 30, 45, 60 min). The autoclave was then cooled to room temperature using tap water.



**Fig. 1.** Structure of a 1-L autoclave: 1. Stirring Motor; 2. Gas Port; 3. Heating Furnace; 4. Stirrer; 5. Cooling Pipe; 6. Autoclave; 7. Sampling Port; 8. Pressure Sensor; and 9. Temperature Probe

After each run, the gas was vented into an airbag and the autoclave contents were poured into a vessel. The procedure for separating the liquid products is shown in Fig. 2. The aqueous phase was first filtered to remove the water-insoluble fraction. The filtered aqueous solution was then extracted three times with dichloromethane (DCM). Next, the DCM solution was evaporated at 28 °C with a rotary evaporator, and the residue obtained was called Oil-1. The DCM-insoluble fraction was extracted three times with ethyl acetate (EA) before the EA solution was concentrated *in vacuo* at 40 °C to obtain a residue that was called Oil-2. The EA-insoluble fraction was termed Organics Dissolved (OD), and was evaporated at 70 °C. The water-insoluble fraction and wall of the autoclave were washed with acetone three times, and the contents were separated by filtration. The acetone solution was evaporated at 35 °C using a rotary evaporator, and the residue obtained was called heavy oil (HO). The acetone-insoluble fraction was dried at 105 °C to obtain the remaining reaction residue. The experiments were repeated two times and the deviation of the liquid yields are within  $\pm$  1%.



**Fig. 2.** Procedure for separating the liquefaction products

### Analysis Method

The compositions of Oil-1, Oil-2, and HO were analyzed by a gas chromatograph (GC) equipped with a selective detector (Agilent 6890-5975i, Agilent Technologies, California, American) after dissolved in the corresponding extraction solvent again. Before we proceed with the GC-MS analyzing, the Oil-1 was dissolved in 50 mL of dichloromethane, the Oil-2 was dissolved in 50 mL of ethyl acetate, and HO was dissolved in 100 mL of acetone, and then 1 mL of the solution was taken from the chromatogram vial for GC-MS test. Both the injector and detector were kept at 250 °C with a He carrier gas velocity of 1.0 mL/min. An HP-INNOWax column (Agilent 19091N-136, 60.0 m × 0.25 mm × 0.25 μm) was used. For good product separation, the oven was programmed as follows: 5 min isothermal at 50 °C, followed by a heating rate of 5 °C/min to reach 250 °C, and this final temperature was held for 30 min. The sample injection volume was set to 1.0 μL. Data were acquired and processed using the Chemstation software (Agilent Technologies, California, USA). The compounds were identified by comparing the mass spectra obtained against the National Institute of Standards and Technology (NIST) library data. The gaseous products were analyzed by a GC (Agilent 6890, Agilent Technologies, California, USA) equipped with a thermal conductivity detector (TCD). He and H<sub>2</sub> were used as the carrier and detector gases, respectively, at a flow rate of 45 mL/min. The inlet temperature was 100 °C and the detector temperature was 200 °C.

## Data Interpretation

The product yields were calculated based on the dry mass of the initial biomass with Eqs. 1 and 2:

$$Y_X = (M_X / M_{\text{biomass}}) \times 100\% \quad (1)$$

$$Y_{\text{Total oil}} = Y_{\text{Oil-1}} + Y_{\text{Oil-2}} + Y_{\text{HO}} \quad (2)$$

In the formula,  $Y_X$  stands for the yield of Oil-1, Oil-2, HO, Gas, OD, or Residue;  $M_X$  represents the mass of the substances dissolved in DCM ( $M_{\text{DCM-soluble}}$ , g), EA ( $M_{\text{EA-soluble}}$ , g), acetone ( $M_{\text{acetone-soluble}}$ , g), or represents the mass of the substances could not dissolve in EA ( $M_{\text{EA-insoluble}}$ , g), acetone ( $M_{\text{acetone-insoluble}}$ , g);  $M_{\text{biomass}}$  represents the mass of the sugarcane bagasse (g), Gas (g);  $Y_{\text{Total oil}}$  stands for the yield of total oil.

The high heating value (HHV) of the total bio-oil was computed based on the Dulong formula (Tekin *et al.* 2014):

$$\text{HHV (MJ/kg)} = 0.3383 C + 1.422*(H-O/8) \quad (3)$$

In the formula, C, H, and O represent the weight percentages of carbon, hydrogen, and oxygen, respectively.

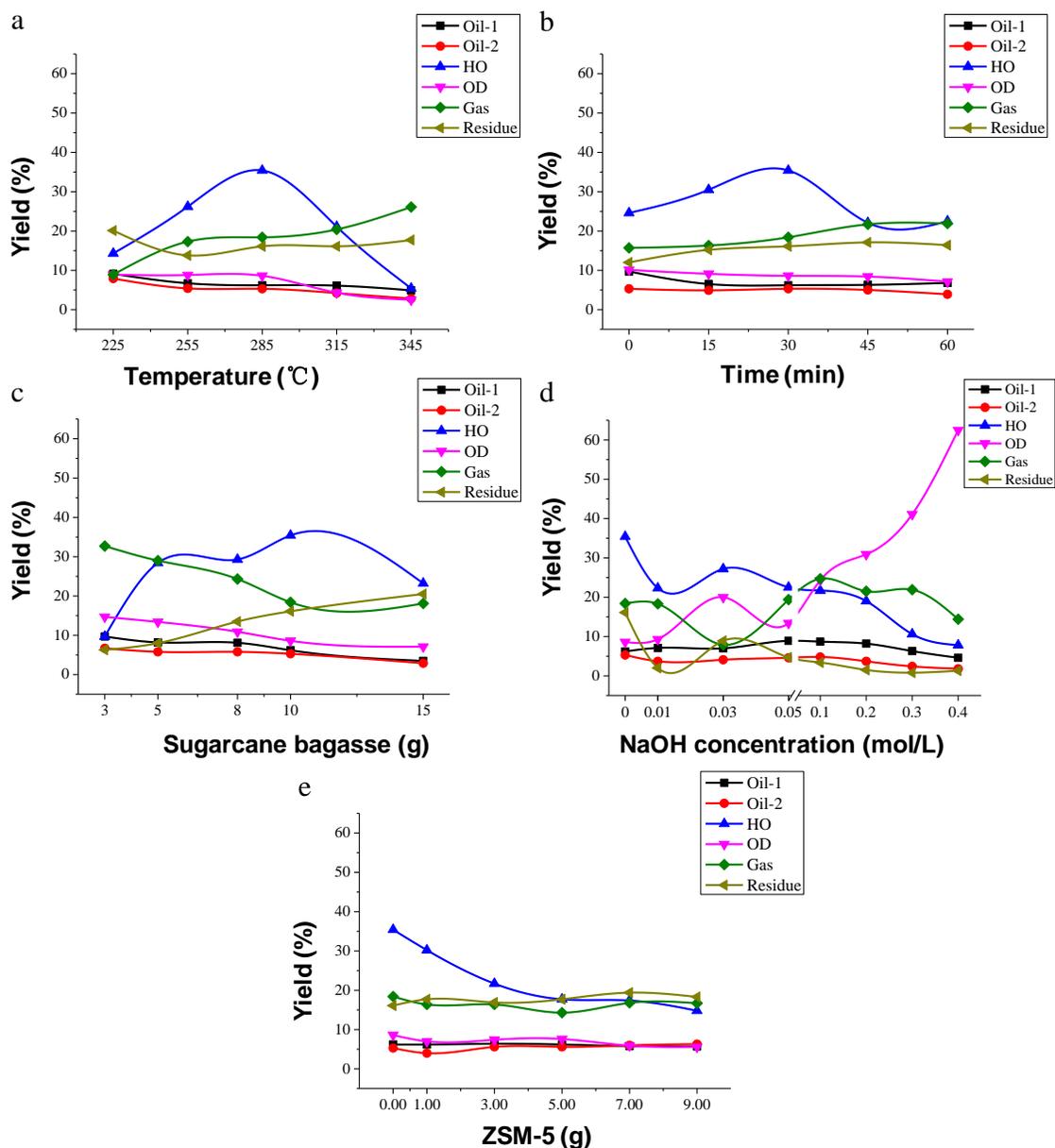
## RESULTS AND DISCUSSION

To investigate the effects of the reaction conditions (temperature, time, biomass/water ratio, NaOH concentration, and ZSM-5 amount) on the oil yields, a total of 25 runs were carried out in this work. The results are summarized in Fig. 3, which provided extensive information on the conditions used during HTL of sugarcane bagasse.

### Effect of the Reaction Temperature

Experimental studies have been conducted on sugarcane bagasse in the HTL in the temperature ranging from 225 to 345 °C in 30 min. As shown in Fig. 3, the HO yield initially increased from 14.3% to 35.4% as the reaction temperature was increased from 225 to 285 °C. More biomass was converted to HO when the temperature was increased from 225 to 285 °C, and as a result, the residue yield decreased. When the temperature continued to increase to 345 °C, the total oil yield decreased to 13.1%. This was caused by a competition between two different reactions involved in the liquefaction process, hydrolysis and repolymerization.

During the initial stage, the biomass was decomposed and depolymerized into small compounds at a lower temperature, and the molecules may have rearranged through condensation, cyclization, or polymerization reactions to form new compounds as the temperature increased. This suggested that different reactions were dominant during different stages (Beauchet *et al.* 2011). The yields of Oil-1 and Oil-2 decreased steadily with an increasing reaction temperature, while the OD yield decreased slightly between 225 and 285 °C, before decreasing sharply between 285 and 345 °C. The gas yield increased steadily with an increasing reaction temperature, from 8.9% at 225 °C to 26.1% at 345 °C, which may have been caused by the formation of gases from secondary decomposition reactions and the Boudouard reaction that were activated at high temperatures (Abu El-Rub *et al.* 2004).



**Fig. 3.** Yields of the liquefaction products under different conditions: (a) 10 g of sugarcane bagasse, 200 mL of distilled water, 30 min; (b) 10 g of sugarcane bagasse, 200 mL of distilled water, 285 °C; (c) 30 min, 200 mL of distilled water, 285 °C; (d) 10 g of sugarcane bagasse, 30 min, 200 mL of NaOH, 285 °C; and (e) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 285 °C

The influence of the temperature on the yield of liquefaction products appeared to be sequential. Initially, the rise in temperature benefited the bio-oil yield. After reaching a maximum yield, any further increase in temperature inhibited biomass liquefaction. In general, very high temperatures were usually not suitable for the production of liquid oils, both in terms of the high operational cost and poor liquid oil yield (Tran 2016). This observation is similar to the research of Gai *et al* (2015), who reported that the yields of bio-oil decreased when the temperature exceeded the specific point (300 °C). The maximum total oil yield (46.9%) was obtained at 285 °C under the experimental conditions

reported in this work, and the biomass conversion was 83.9%, which is similar to the biomass conversion (83.9%) with a mixed solvents ethanol /water (Kosinkova *et al.* 2015). A higher total oil yield was obtained with water as solvent than with tetralin/water (35.0%) (Li *et al.* 2015).

### Effect of the Reaction Time

The effect of the reaction time on the yield of each product for the conditions of 285 °C, 10 g of sugarcane bagasse, and 200 mL of distilled water are shown in Fig. 3. The HO yield initially increased from 0 to 30 min, before decreasing when the reaction time further increased. This was mainly because the condensation and repolymerization of intermediates that formed residues, and secondary decomposition reactions that formed gaseous products after prolonging the reaction time (Yin and Tan 2012). The residue yield increased slightly with the reaction time, from 12.0% at 0 min to 16.4% at 60 min, while the gas yield increased from 15.7% at 0 min to 21.9% at 60 min. The OD yield decreased slightly from 10.1% at 0 min to 7.1% at 60 min. It was concluded that to liquefy sugarcane bagasse in water and obtain the highest HO and total oil yields, a reaction time of 30 min is sufficient.

### Effect of the Biomass/Water Ratio

Figure 3 shows the change in the product yields for the different biomass/water ratios when the reaction was heated at 285 °C for 30 min. Over the ratio range of 3 g/200 mL to 10 g/200 mL, the HO yield initially increased with the biomass/water ratio, but quickly decreased thereafter. While the yields of Oil-1, Oil-2, and OD decreased gradually with an increasing biomass/water feedstock ratio, the residue yield exhibited the opposite trend and increased from 6.3% to 20.5% over the biomass/water feedstock ratio range of 3 g/200 mL to 15 g/200 mL. The authors found it reasonable that the compositions of the reaction products varied with each biomass/water ratio. The results showed that a high biomass/water feedstock ratio was usually not suitable for the liquefaction of sugarcane bagasse. This observation is similar to the report of Wang *et al.* (2008), who observed that high biomass/water feedstock ratio increased the amount of leftover residues due to decrease in solvation for biomass components. Boocock and Sherman (1985) reported the low water/wood ratios affect the chemical role of water in breaking down the wood structure. The production of liquid oils at a biomass/water ratio of 10 g/200 mL was sufficient to give the highest HO and total oil yields.

### Effect of the NaOH Concentration

The NaOH concentration was also an important factor that affected the oil yields. Figure 3 shows the results of different NaOH concentrations (0.01, 0.03, 0.05, 0.10, 0.20, 0.30, and 0.40 mol/L) during HTL with 10 g of sugarcane bagasse and 200 mL of NaOH solution at 285 °C for 30 min. NaOH had an important influence on the decomposition of the sugarcane bagasse, and it affected both the bio-oil yield and product conversion. When NaOH was used as a catalyst, the bio-oil and residue yields decreased, while the OD yield increased as the NaOH concentration increased. The low bio-oil yield indicated that cellulose was degraded into more water-soluble products during HTL. The reduction of the residue yields demonstrated that the addition of NaOH accelerated the collapse of intramolecular and intermolecular hydrogen bonds in the sugarcane bagasse structure, and catalyzed the reduction and cracking reactions of macromolecules (Li *et al.* 2015). The ionization constant of water increased with the temperature and reached a maximum at

approximately 250 °C. The amount of dissociation at 250 °C was three times what it is at an ambient temperature and pressure (Singh *et al.* 2013). Therefore, subcritical water in the 220 to 300 °C temperature range can work as a benign solvent, as well as a self-neutralizing catalyst. In this range, water acts as both a reactant and reaction medium. As a reactant, water facilitates hydrolysis reactions and rapidly degrades the polymeric structure of biomass to water-soluble products (Kumar 2010; Ju *et al.* 2011). The ionization constant was significantly increased as the NaOH concentration increased, which promoted the hydrolysis of sugarcane bagasse to water-soluble products. This explained why the OD yield increased remarkably with the NaOH concentration and some valuable substances could be recovered from the OD. These results showed that the alkalinity of the hydrothermal agent had a major effect on the conversion rate of biomass.

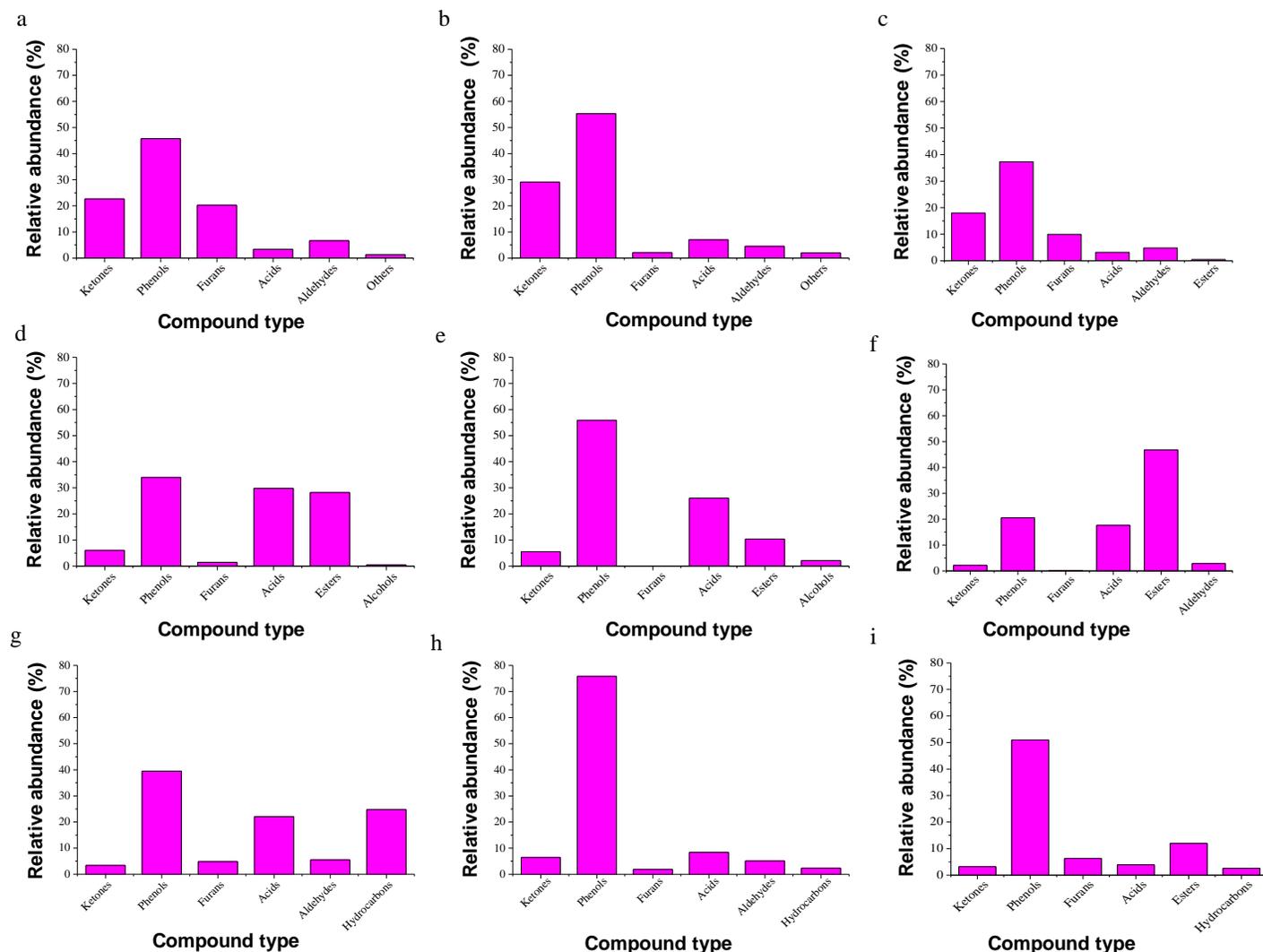
At the same time, the Oil-1 yield increased with the NaOH concentration and reached a maximum value of 8.9% at a NaOH concentration of 0.05 mol/L, which was 1.44 times greater than the yield obtained from an uncatalyzed reaction. A further increase in the NaOH concentration inevitably led to a decrease in the Oil-1 yield. The yield of Oil-2 showed the same trend as that of Oil-1. Therefore, higher NaOH concentrations were in favor of biomass hydrolysis.

### Effect of the ZSM-5

Figure 3 showed the effects on the product yields for different amounts of ZSM-5 (1.00, 3.00, 5.00, 7.00, and 9.00 g). The maximum Oil-1 yield was 6.4% when the amount of ZSM-5 was 3.00 g. The Oil-1 yield then decreased as the ZSM-5 amount increased. While the Oil-2 yield increased gradually with an increasing amount of ZSM-5, from 4.0% at 1.00 g to 6.3% at 9.00 g, the HO and total oil yields exhibited the opposite trend. The OD yield initially increased with an increased amount of ZSM-5, from 7.0% at 1.00 g to 7.6% at 5.00 g, and then decreased to 5.6% at 9.00 g. It was possible that ZSM-5 deoxidized some of the oxygen-containing compounds in the OD to produce Oil-1 and Oil-2, which resulted in a decrease in the OD yield while increasing the yield of Oil-1 and Oil-2. The residue yield decreased with an increasing amount of ZSM-5, from 17.7% at 1.00 g to 16.9% at 3.00 g, and then increased to 18.3% at 9.00 g. This is because too many ZSM-5 was used, the pore channel was easily blocked, and catalyst activation was decreased. (Ding *et al.* 2015). The results showed that more ZSM-5 was sufficient to increase the residue yield, but was not suitable for the liquefaction of sugarcane bagasse. The ideal amount of ZSM-5 was 3.00 g.

### Analysis of the Bio-Oil

Bio-oil is a complex mixture and was characterized by gas chromatography-mass spectrometry (GC-MS). The mixture was separated and the main oil constituents were successfully detected, which indicated that both the columns and analysis conditions used were appropriate. However, the upper temperature limit of the GC column was 250 °C, which limited the analysis and testing of components with high boiling points. In this study, the GC-MS analysis of the bio-oil was used mainly for small molecules with low boiling points. Tables 2, 3, and 4 show that the products of oxygenation (phenols, acids, ketones, alkenes, and esters) were abundant in the bio-oil for different reaction conditions, and there were plenty of hydroxyl groups in the cellulose. Phenols are generally formed by dehydration, isomerization, and cyclization reactions (Chen *et al.* 2016). The change in the bio-oil composition under different catalysts is shown in Fig. 4, and the different catalyst concentrations are shown in Fig. 5.



**Fig. 4.** Oil-1 composition: (a) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 285 °C; (b) 10 g of sugarcane bagasse, 30 min, 200 mL of 0.03 mol/L NaOH, 285 °C; and (c) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 3.00 g of ZSM-5, 285 °C  
 Oil-2 composition: (d) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 285 °C; (e) 10 g of sugarcane bagasse, 30 min, 200 mL of 0.03 mol/L NaOH, 285 °C; and (f) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 3.00 g of ZSM-5, 285 °C  
 HO composition: (g) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 285 °C; (h) 10 g of sugarcane bagasse, 30 min, 200 mL of 0.03 mol/L NaOH, 285 °C; and (i) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 3.00 g of ZSM-5, 285 °C

**Table 2.** Relative Abundances of the Various Compound Types in Oil-1 (%)

Parameters	Temperature (°C)	Ketones	Phenols	Furans	Acids	Aldehydes	Others
Run 1	225	5.8	9.4	57.6	2.8	4.5	0.9
	255	13.8	20.8	24.1	4.4	5.9	1.4
	285	16.2	32.8	14.5	2.4	4.8	0.9
	315	20.4	36.7	6.4	3.1	1.8	1.5
	345	21.8	38.9	4.1	1.0	1.2	0.6
Time (min)							
Run 2	0	10.6	11.9	33.4	4.1	4.4	1.8
	15	15.6	24.2	23.3	2.6	6.7	1.6
	30	16.2	32.8	14.5	2.4	4.8	0.9
	45	18.3	31.4	8.9	2.3	5.8	1.9
	60	19.7	26.9	6.9	5.5	3.8	1.8
Sugarcane Bagasse (g)							
Run 3	3	14.0	27.1	13.4	2.3	8.5	1.5
	5	13.9	25.9	15.7	1.9	7.2	1.5
	8	18.0	28.6	16.6	2.4	5.7	1.4
	10	16.2	32.8	14.5	2.4	4.8	0.9
	15	17.4	33.6	8.6	3.9	4.4	1.1

Run 1: Water: 200 mL, Sugarcane Bagasse: 10 g, Time: 30 min

Run 2: Water: 200 mL, Sugarcane Bagasse: 10 g, Temperature: 285 °C

Run 3: Water: 200 mL, Temperature: 285 °C, Time: 30 min

**Table 3.** Relative Abundances of the Various Compound Types in Oil-2 (%)

Parameters	Temperature (°C)	Ketones	Phenols	Furans	Acids	Esters	Alcohols
Run 1	225	0.6	3.1	41.1	32.9	12.9	0.6
	255	2.1	11.5	11.8	43.3	19.6	0.9
	285	5.4	30.6	1.3	26.9	25.4	0.5
	315	1.6	33.9	0.1	39.5	15.5	0.9
	345	0.5	41.9	0.1	27.9	16.2	-
Time (min)							
Run 2	0	2.1	6.1	26.1	31.7	16.1	0.9
	15	5.1	20.2	9.2	23.8	21.7	0.8
	30	5.4	30.6	1.3	26.9	25.4	0.5
	45	4.1	27.9	0.4	26.8	27.7	0.7
	60	2.3	18.5	0.2	45.3	21.9	0.5
Sugarcane Bagasse (g)							
Run 3	3	2.7	13.9	2.9	13.2	47.3	0.5
	5	2.6	19.4	3.9	18.6	34.4	0.7
	8	4.4	24.1	1.9	24.1	28.5	0.7
	10	5.4	30.6	1.3	26.9	25.4	0.5
	15	4.4	32.8	0.4	21.5	22.9	0.7

**Table 4.** Relative Abundances of the Various Compound Types in HO (%)

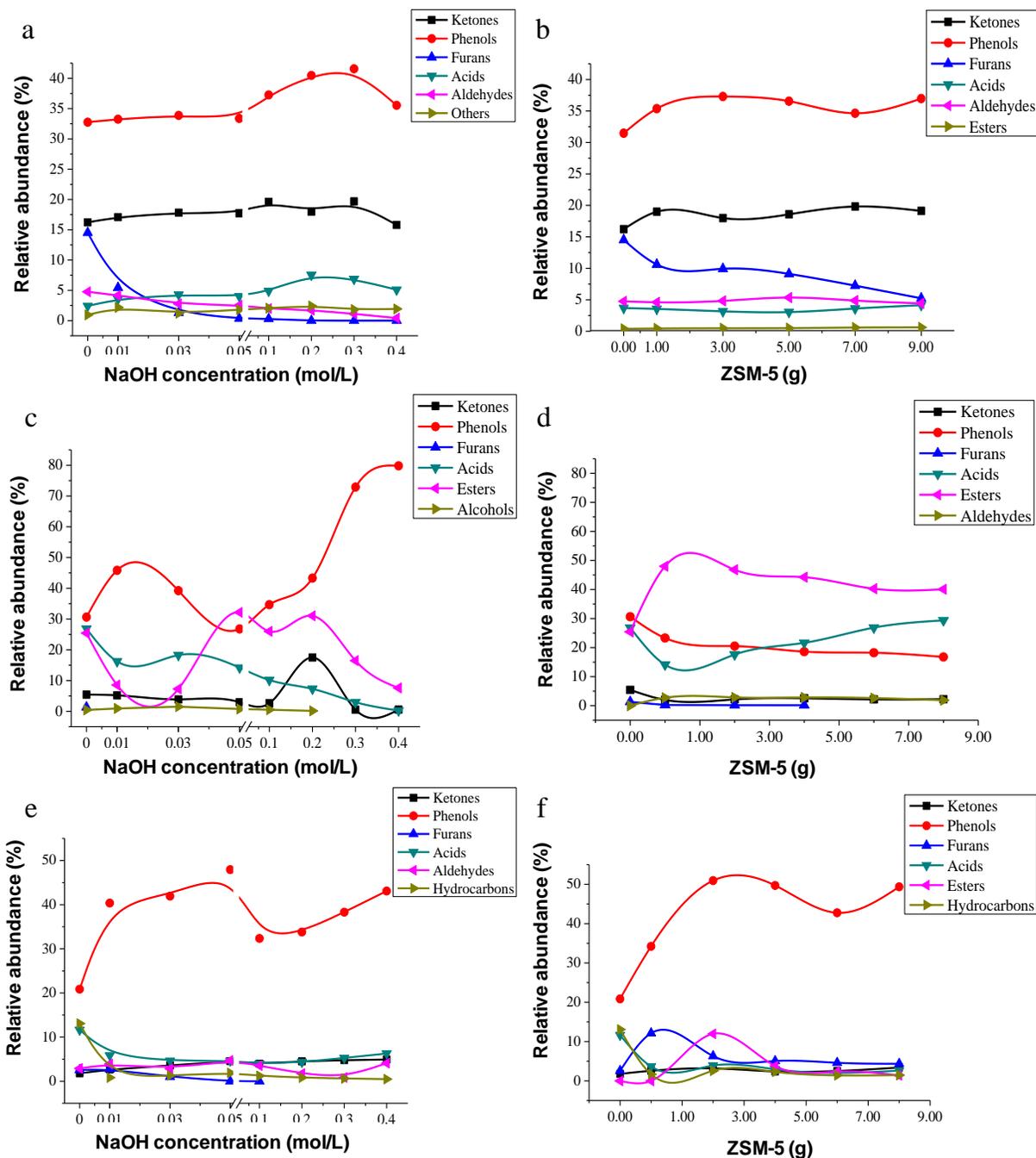
Parameters	Temperature (°C)	Ketones	Phenols	Furans	Acids	Aldehydes	Hydrocarbons
Run 1	225	0.4	6.3	29.3	5.7	12.9	16.5
	255	1.3	12.4	12.8	10.4	5.1	18.3
	285	1.8	20.9	2.6	11.6	2.9	13.1
	315	3.7	24.8	2.9	9.1	1.2	15.3
	345	5.1	27.4	0.7	6.4	0.8	11.4
Time (min)							
Run 2	0	1.0	14.3	20.9	10.0	3.3	13.7
	15	1.5	22.7	7.6	11.0	5.6	12.4
	30	1.8	20.9	2.6	11.6	2.9	13.1
	45	2.7	23.2	2.1	12.1	2.6	14.8
	60	2.5	22.8	2.0	12.8	2.9	15.1
Sugarcane Bagasse (g)							
Run 3	3	0.1	10.3	3.9	6.6	5.7	19.1
	5	0.7	15.9	3.8	6.7	4.9	16.1
	8	1.6	44.3	3.7	9.2	4.4	13.9
	10	1.8	20.9	2.6	11.6	2.9	13.1
	15	3.1	35.9	3.2	7.9	1.4	13.1

#### Products of oil-1

Oil-1 contained a large number of different chemical compounds that were mainly esters, phenols, acids, ketones, alkenes, and furfurals, along with their respective derivatives. The major components of Oil-1 were obtained under different reaction temperatures, and were determined by GC-MS analysis.

As shown in Fig. 4a, the compounds in Oil-1 (285 °C) were grouped according to their relative abundances. Oil-1 contained a large amount of phenols, ketones, aldehydes, and acids, which made it strongly hydrophilic. The bio-oil also had a high water content, which was difficult to separate out. Additionally, Oil-1 had a high content of furan compounds, but a limited amount of esters and alcohols. It is generally believed that acids, ketones, alcohols, esters, and furans are derived from cellulose and hemicellulose liquefied products, whereas the secondary products, phenols and aromatic compounds, are produced from lignin degradation (Cheng *et al.* 2010; Meryemoğlu *et al.* 2014). With the addition of NaOH, more phenols and ketones were obtained because the alkaline solution helped to decompose the lignin fraction into low molecular weight phenolic compounds (Fig. 4b) (Wang *et al.* 2012; Singh *et al.* 2013). The other compounds in Oil-1 were mainly composed of esters, alcohols, and ethylene oxide. When ZSM-5 was used as the catalyst, only 4-methyl-butyrolactone and other ester compounds were detected, and the amount of acids was reduced. This showed that most of the acids are likely converted into esters under catalytic conditions of ZSM-5 (Fig. 4c) (Veses *et al.* 2015).

As the temperature increased (Table 2), the relative amounts of phenols, ketones, furans, acids, and aldehydes in Oil-1 changed accordingly. The relative abundance of furans was greatly influenced by the reaction temperature. The relative abundance decreased as the temperature increased. The relative abundances of the ketone and phenol compounds increased steadily as the reaction temperature increased. Based on the cellulose and hemicellulose hydrothermal degradation pathways, it was evident that a noticeable amount of furans were obtained at the relatively low temperature of 225 °C. As the reaction temperature increased, these furan compounds were further degraded into ketones and acids (Yu *et al.* 2008).



**Fig. 5.** Oil-1 composition at 10 g of sugarcane bagasse, 30 min reaction time, 200 mL of distilled water, and 285 °C with different catalysts: (a) NaOH and (b) ZSM-5; Oil-2 composition at 10 g of sugarcane bagasse, 30 min reaction time, 200 mL of distilled water, and 285 °C with different catalysts: (c) NaOH and (d) ZSM-5; HO composition at 10 g of sugarcane bagasse, 30 min reaction time, 200 mL of distilled water, and 285 °C with different catalysts: (e) NaOH and (f) ZSM-5

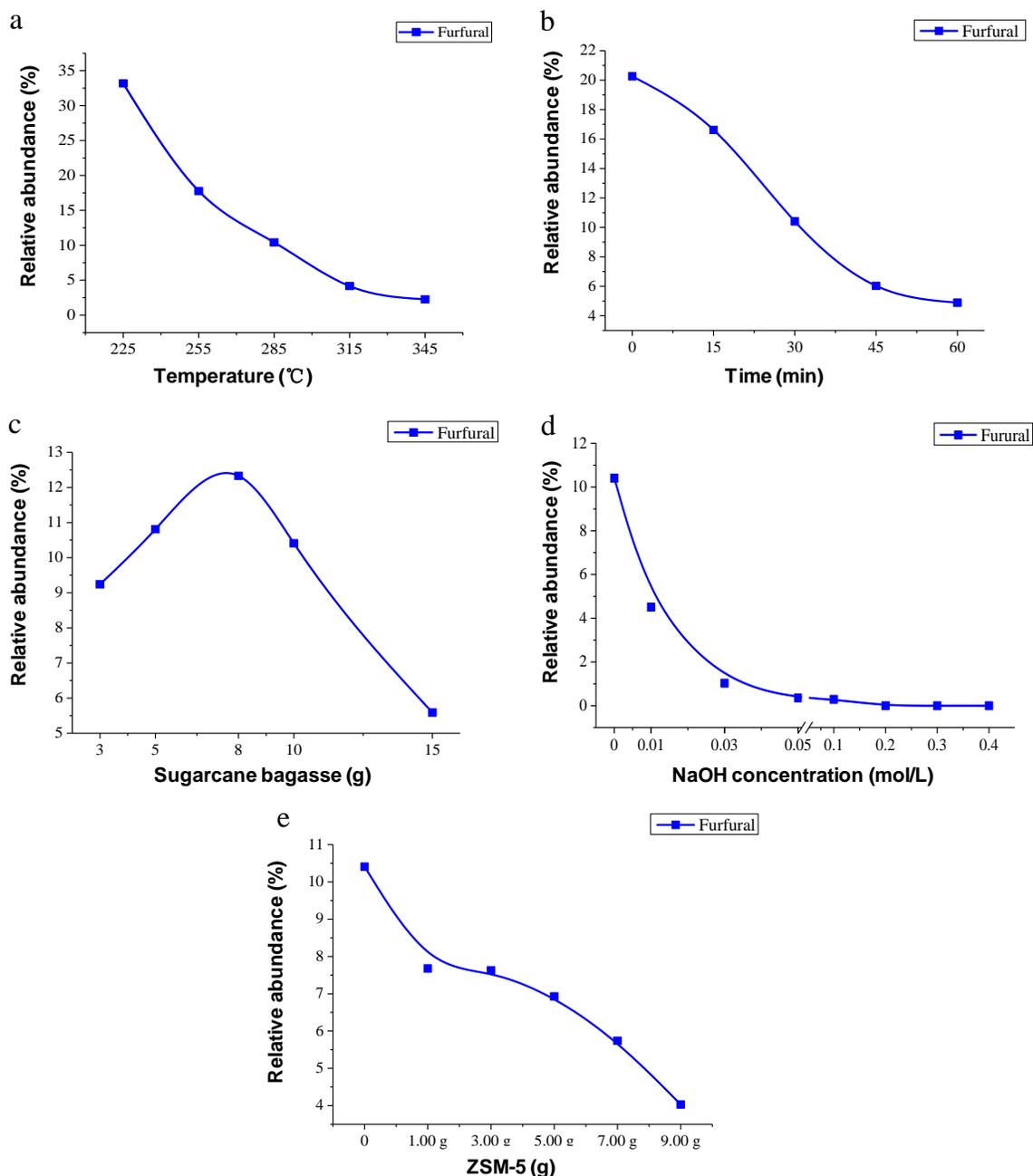
In general, phenols are mainly obtained from lignin hydrothermal degradation, which was inefficient at 225 °C, and so relatively few phenol compounds were obtained. The rate of lignin degradation was accelerated at higher temperatures, and it was observed

that the relative abundance of the phenols reached 32.8% when the temperature increased to 285 °C. However, relative abundance of the phenols changed little beyond this temperature, which indicated that the lignin might have been substantially degraded at 285 °C. The influence of the reaction time on the relative abundance of the various compounds in Oil-1 was also similar to that of the reaction temperature. While the reaction time was positively correlated to the peak area ratio of the phenols, a prolonged reaction time adversely affected the relative abundance of the furans. The biomass/water feedstock ratio had less of an impact on the relative abundance of the various compounds in Oil-1 compared with the reaction temperature and time. In Figs. 5a and 5b, the relative abundance of furans was mostly affected by the NaOH concentration and ZSM-5 amount. The relative abundance of the furans was recorded as 14.5% without a catalyst. However, when the NaOH concentration exceeded 0.20 mol/L, no furan compounds were detected in Oil-1. Also, the content of furans decreased from 14.5% at 0.00 g to 5.24% at 9.00 g as the amount of ZSM-5 increased.

Furfurals that formed *via* the degradation of carbohydrates are important intermediates produced during the HTL of biomass (Sinağ *et al.* 2010, 2012). Hydroxymethyl furfural (HMF), methyl furfural (MF), and furfural (2-furaldehyde) were the different types of furfurals that were formed, while 5-HMF was the conversion product of D-fructose. MF and furfural were both hydrothermolysis products of 5-HMF (Thananathanachon and Rauchfuss 2010). The relative abundance of the furfurals for different conditions are shown in Fig. 6. A higher reaction temperature and longer reaction time were unfavorable for the production of furfurals. The relative abundance of the furfurals decreased sharply from 33.2% at 225 °C to 2.3% at 345 °C. When the reaction time increased from 0 to 60 min, the relative abundance of the furfurals decreased from 20.3% to 4.9%. The best biomass/water feedstock ratio for producing furfurals was 8.00 g/200 mL. There was a noticeable change in the yield of furfurals before and after adding NaOH as a catalyst. At 0.01 mol/L NaOH, the furfurals yield was only 4.5%, which was lower than the 10.4% yield obtained without using a catalyst. Furfurals were no longer detected when the NaOH concentration reached 0.20 mol/L. Fewer furfurals were also obtained with the addition of ZSM-5. It was obvious that NaOH and ZSM-5 promoted further decarburation and other chemical reactions of furfurals compounds to formation phenolic compounds (Li *et al.* 2013). Therefore, they were unfavorable for furfural generation.

#### *Products of oil-2*

In comparison with Oil-1, the products of Oil-2 contained fewer compounds and were mainly composed of acids, phenols, ketones, and furfurals, along with their derivatives. As shown in Fig. 4d, the compounds in Oil-2 (obtained at 285 °C) were categorized into different chemical groups according to their relative abundances. The main components of Oil-2 included phenols, acids, esters, and ketones. In comparison with Oil-1, Oil-2 contained a large amount of acids and esters, which was probably because they are more soluble in EA than DCM, according to the principle of similar miscibility. In Fig. 4e, furans were not detected, which showed that NaOH was detrimental to the formation of furans in both Oil-1 and Oil-2. ZSM-5 obviously affected the compounds generated in Oil-2 and majorly reduced the formation of ketones, phenols, furans, acids, and alcohols. However, the amount of esters generated increased and aldehydes were detected as well (Fig. 4f).



**Fig. 6.** Peak area ratios of furfurals under different conditions: (a) 10 g of sugarcane bagasse, 200 mL of distilled water, 30 min; (b) 10 g of sugarcane bagasse, 200 mL of distilled water, 285 °C; (c) 30 min, 200 mL of distilled water, 285 °C; (d) 10 g of sugarcane bagasse, 30 min, 200 mL of NaOH, 285 °C; and (e) 10 g of sugarcane bagasse, 30 min, 200 mL of distilled water, 285 °C

Table 3 shows that there were some fluctuations in the amount of acids. It was possible that the acids and esters were interconverted at different reaction temperatures. Ester species can weaken the acidity, corrosiveness, and stability of bio-oils (Li *et al.* 2016). Based on Table 3, achieving an optimum temperature, reaction time, and biomass/water ratio was important for the formation of esters. Under similar conditions, the lower content of acids was advantageous to the bio-oil, as large amounts of acid not only accelerated Oil-

2 deterioration, but also made the oil prone to corrosion over the course of internal combustion.

Also, Table 3 shows that the peak area ratios of the acids and furans noticeably changed with the temperature and reaction time. When the reaction time increased from 0 to 15 min, the relative abundance of the acids decreased from 31.7% to 23.8%, and then increased to 45.3% at 60 min. The relative abundance of the furans decreased sharply with the reaction temperature and time. When the reaction temperature increased from 225 to 285 °C, the relative abundance decreased from 41.1% to 1.3%. Meanwhile, increasing the reaction time from 0 to 30 min led to a decrease in the relative abundance of the furans from 26.1% to 1.3%, which then decreased further to 0.2% at 60 min. Similar to furfurals, higher reaction temperatures and longer reaction times were unfavorable for the generation of furans. Small molecular carboxylic acids were mainly produced by the degradation of polysaccharides and cellulose, and these acid molecules were then decomposed or rearranged through condensation, cyclization, or polymerization reactions and formed new compounds as the reaction time increased (Srokol *et al.* 2004). Yang *et al.* (2014) suggested that furfurals, such as 5-HMF, could easily produce acetic acid *via* an oxidation process. This may have been the reason why the acid yield increased when the reaction time exceeded 45 min. Based on Table 3, the phenols and esters were negatively correlated with each other. Because the major substance in esters is dibutyl phthalate, which is transformed from a phenolic monomer, it was possible for esters to decompose into phenols with NaOH (Kang *et al.* 2013). On the other hand, high NaOH concentrations promote the  $\beta$ -aromatic bond and the ether bond of the lignin to break down to form the phenolic compound (Gao 2013). High NaOH concentrations were not conducive to the formation of esters, but were beneficial to the generation of phenolic compounds instead (Fig. 5c). In Fig. 5d, ZSM-5 showed remarkable effects on Oil-2 as the amount of ZSM-5 increased from 0.00 to 1.00 g. The amount of esters rapidly increased from 25.43% to 47.99%, and then decreased. The acid yield exhibited the opposite trend. It decreased from 27.67% to 14.53%, and then increased to 30.28%. As the amount of ZSM-5 increased, the amount of phenols, furans, and ketones decreased. The decrease of the oxygenated compounds is a result of dehydration and decarboxylation reactions. The oxygen is removed in the form of water vapour, CO<sub>2</sub> and CO (Thring *et al.* 2000).

### *Products of HO*

The HO yield had a noticeable influence on the total oil yield. Its compounds were mostly oxygen-containing unsaturated hydrocarbon derivatives with carbon atoms numbering between 2 and 21, which included acids, phenols, and some non-polar aromatic compounds, as well as aliphatic compounds. As shown in Fig. 4g, the compounds in HO (285 °C) were categorized into different chemical groups according to their relative abundances. It was evident that HO had a relatively high content of hydrocarbons, which was different from Oil-1 and Oil-2. With the addition of NaOH, the amounts of acids and aldehydes in the HO decreased. The effects of the temperature, reaction time, and biomass/water ratio on the relative abundance of hydrocarbons in the HO were comparatively small (Table 4). In contrast, phenols and furans were affected in a major way by the reaction conditions, which was consistent with the results of the compositional analysis of Oil-1 and Oil-2. Phenols were the main compounds in the HO after the addition of NaOH (Fig. 4h), and they were mainly present in the sugarcane bagasse as 4-ethyl-phenol, 2, 6-dimethoxy-phenol, and phenol. As can be seen in Figs. 4i and 5f, ZSM-5 greatly reduced the relative abundances of acids and hydrocarbons in the HO. Without

ZSM-5, esters were not detected in the HO. When the amount of ZSM-5 was increased to 3.00 g, the peak area ratio reached 11.97%. In general, most of the acids were likely converted into esters after the addition of a catalyst (Tang *et al.* 2009). Also, phenols were the main compounds in the HO, and ZSM-5 facilitated the generation of these compounds.

The relative abundance of the phenols increased as the concentration of NaOH increased from 0.01 to 0.03 mol/L (Fig. 5e). In general, phenols are derived from the decomposition of lignin. Barbier *et al.* (2012) proposed that lignin first decomposes into methoxylated benzenes, and subsequently decomposes into oxygenated hydrocarbons. The oxygenated hydrocarbons could have been rearranged through condensation, cyclization, or polymerization reactions to obtain hydroxylated and methoxylated benzenes. Hsieh *et al.* (2009) previously used NaOH to pretreat rice hulls (pH = 11.5 to 11.7) and showed that 73% of the holocellulose and 42% of the lignin remained in the precipitate, which indicated that NaOH was beneficial to the decomposition of lignin at low concentrations. The relative abundance of the phenols decreased sharply when the concentration increased to 0.05 mol/L. This could have been because of the fact that NaOH promotes the decomposition of methoxylated benzenes into oxygenated hydrocarbons, such as acetic acid (Nazari *et al.* 2015). At NaOH concentrations higher than 0.10 mol/L, the relative abundance of the phenols noticeably increased. High NaOH concentrations prohibited the decomposition of methoxylated benzenes into oxygenated hydrocarbons and/or promoted the rearrangement of oxygenated hydrocarbons into hydroxylated and methoxylated benzenes. The basic building blocks of lignin are transp-coumarylalcohol, coniferyl alcohol, and sinapyl alcohol. In the HTL with NaOH, various phenols and methoxy phenols are formed by hydrolysis of ether-bonds, and then degrade by hydrolysis of methoxy groups; however, the benzene ring is stable at these conditions (Liu *et al.* 2006).

### Elemental analysis

Table 5 shows the elemental analysis of sugarcane bagasse and the total bio-oil obtained from sugarcane bagasse in HTL at 285°C in non-catalyst and different catalysts. It can be seen that after sugarcane bagasse had been converted to bio-oil, a significant reduction in oxygen content can be observed. And the oxygen content in the total bio-oil was effectively reduced and O/C was lower with catalysts. Among the catalysts, NaOH was able to effectively deoxygenate, as the total bio-oil contained 21.66 wt% of oxygen. ZSM-5 increased the hydrogen content and H/C, thereby increasing the HHV of the total bio-oil. The higher HHV and lower oxygen content with catalysts makes a better quality than with non-catalyst. Taken together, sugarcane bagasse in HTL with catalysts not only significantly reduced the yield residue, the quality of bio-oil also be improved as the oxygen content decreased and the HHV increased.

**Table 5.** Elemental Analysis of Total Bio-oil Obtained from Sugarcane Bagasse in HTL at 285°C in Non-catalyst and Different Catalysts

Catalyst	Elemental composition (wt%)			HHV (MJ/kg)	O/C (molar ratio)	H/C (molar ratio)
	C	H	O			
Sugarcane bagasse	44.70	5.30	47.60	17.13	0.80	1.42
Non-catalyst	63.03	6.31	24.24	25.98	0.29	1.20
NaOH	63.74	6.51	21.66	26.97	0.25	1.22
ZSM-5	64.09	7.35	23.72	27.91	0.28	1.38

## Analysis of Gaseous Products

The gaseous products were analyzed by GC-TCD and consisted mainly of CO<sub>2</sub>, as well as smaller amounts of CO, H<sub>2</sub>, CH<sub>4</sub>, and short-chained alkanes. It was clear that the temperature remarkably affected the H<sub>2</sub> and CH<sub>4</sub> contents from 225 to 345 °C. The proportion of H<sub>2</sub> in the gaseous products was 2.31% at 345 °C, which was more than ten times higher than the value recorded at 225 °C (0.19%). Meanwhile, the content of CH<sub>4</sub> increased from 1.35% at 225 °C to 5.46% at 345 °C. In contrast, the effect of the reaction time on the H<sub>2</sub> and CH<sub>4</sub> contents was not as obvious as the effect of the reaction temperature. The content of H<sub>2</sub> increased with the reaction time, and it reached a maximum value of 1.29% at 30 min. The content of CH<sub>4</sub> in the gaseous products generally increased with the reaction time, from 3.07% at 0 min to 4.41% at 60 min. The content of CH<sub>4</sub> displayed a strong positive correlation as the amount of sugarcane bagasse increased from 3 to 15 g. The results showed that a high biomass/water ratio was good for producing CH<sub>4</sub>. However, the content of H<sub>2</sub> in the gaseous products slightly decreased with an increasing amount of sugarcane bagasse, from 1.34% at 3 g of sugarcane bagasse to 0.92% at 15 g of sugarcane bagasse.

It was clear that the effect of the NaOH concentration on the CH<sub>4</sub> content was major. The CH<sub>4</sub> content initially increased as the NaOH concentration increased from 0.01 to 0.40 mol/L, and then it decreased when the NaOH concentration continued to increase. At a NaOH concentration of 0.20 mol/L, the content of CH<sub>4</sub> in the gaseous products reached 14.41%, which was about four times greater than the value recorded when there was no NaOH present. In contrast, the H<sub>2</sub> content was negatively affected when the NaOH concentration was below 0.40 mol/L. At a NaOH concentration of 0.40 mol/L, the content of H<sub>2</sub> was 2.14%, which was higher than the value recorded in the absence of a catalyst (1.29%).

With the presence of ZSM-5, the content of H<sub>2</sub> decreased from 1.29% to 0.53%. This showed that ZSM-5 reduced the H<sub>2</sub> content, and it further decreased it with an increasing amount of ZSM-5. The content of CH<sub>4</sub> exhibited the opposite trend, and increased from 5.09% to 11.74% when the amount of ZSM-5 increased from 1.00 to 9.00 g. In the absence of ZSM-5, the content of CH<sub>4</sub> was 3.65%. It was determined that ZSM-5 remarkably promoted the formation of CH<sub>4</sub>. A higher amount of ZSM-5 can promote hydrogenation and methanation (Iliopoulou *et al.* 2012).

## CONCLUSIONS

1. When the reaction conditions were 10 g of sugarcane bagasse, 200 mL of distilled water, 30 min, and 285 °C, the maximum bio-oil yield (46.9%) was obtained, and the biomass conversion was 83.9%.
2. In comparison with Oil-1, Oil-2 contained a large amount of acids and esters, which was probably because they are more soluble in EA than DCM. HO extracted with acetone solution had a relatively high content of hydrocarbons.
3. Sugarcane bagasse was more easily converted by HTL into water-soluble compounds in the presence of NaOH. With the addition of NaOH, the residue yield decreased noticeably from 16.1% to 8.9%, and the yield of OD increased, from which some valuable substances could be recovered. These results showed that NaOH accelerated the collapse of intramolecular and intermolecular hydrogen bonds in the sugarcane

bagasse structure, and it catalyzed the reduction and cracking reactions of the macromolecules under relatively mild conditions.

4. With the addition of NaOH, the contents of acids and furfurals in the bio-oil decreased after HTL. The decrease of furfurals shows NaOH promoted further decarburization and other chemical reactions of furfurals compounds to formation phenolic compounds. And NaOH can effectively deoxygenate to improve the HHV.
5. The use of ZSM-5 as the catalyst during HTL improved the properties of the liquid obtained, especially in terms of the oxygen content, and effectively reduced the amount of acidic compounds. ZSM-5 improved the hydrogen content and H/C, thereby enhanced the quality of bio-oil which has a higher HHV.
6. The gaseous products H<sub>2</sub> and CH<sub>4</sub> were remarkably affected by the temperature, NaOH concentration, and ZSM-5 amount.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (51108458), Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2011-1139), and China Scholarship Council (201506445017).

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Article submitted: July 20, 2017; Formatted article: July 26, 2017; Peer review completed: September 17, 2017; Revised version received: November 17, 2017; Accepted: November 18, 2017; Published: December 8, 2017.  
DOI: 10.15376/biores.13.1.997-1018