

Preparation of bio-oil by catalytic pyrolysis of corn stalks using red mud

Wang Shaoqing^{1,2}, Xu Meili^{1,2}, Wang Fang^{1,2}, Li Zhihe^{1,2*}

(1. School of Agricultural Engineering and Food Science, Shandong University of Technology, Zibo 255091, China;

2. Shandong Research Center of Engineering and Technology for Clean Energy, Zibo 255091, China)

Abstract: Red mud is a solid waste residue with alkaline nature (pH>12)-originating from the Bayer process in the production of alumina, which was probed in catalytic pyrolysis to determine its feasibility as a solid catalyst for bio-oil formulation. The red mud was characterized using X-ray fluorescence, XRD (X-ray diffraction), TG-DTG (thermogravimetry-derivative thermogravimetry), BET (surface area and pore size analyzer) measuring and testing techniques. Experiments of non-catalytic and catalytic pyrolysis of 40-60 mesh size corn stalk powder were channelled for bio-oil production in a fixed bed reactor. It was ascertained that adding different proportions of red mud had minute influence on bio-oil production rate and product distribution. The study signaled that liquid yield from the catalytic pyrolysis was lower than that from non-catalytic pyrolysis. Through a series of bio-oil characterization, it was encountered that the most obviously change in the bio-oil from catalytic pyrolysis was significant acidity reduction (pH>4). Meanwhile, the content of ketones and phenols was enhanced. Hence, the co-processing of agricultural waste and by-products alumina industry may offer an economical and environmentally friendly way of catalytic pyrolysis with abbreviating the red mud environmental effects.

Keywords: red mud, catalytic pyrolysis, corn stalk powder, bio-oil

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1 Introduction

Bio-oil originates from the depolymerization and fragmentation of cellulose, hemicelluloses and lignin in biomass under the anaerobic environment with fast pyrolysis^[1]. However, bio-oil comprises more than 300 kinds of compounds, the direct use of bio-oil as fuel may present many contrary and hostile factors due to its high viscosity, corrosiveness, poor heating value, and relative instability^[2]. The main reason for confining bio-oil use

is that it comprises a large number of oxygen-containing organic compounds. Bio-oil can be upgraded by different physical, chemical and catalytical methods^[3]. In this study, we revolve about catalytic pyrolysis to enhance the quality and stability of the bio-oil. Currently, there are two methods to reduce the oxygen content in bio-oil during the process of catalytic pyrolysis. The first one is hydrogen catalytic deoxidization with high pressure or in the presence of hydrogen donor solvents. The second method is using molecular sieve catalyst mix with reaction material, this method is similar to petrochemical-deoxy method, using catalyst for pyrolytic vapors of biomass online processing. In order to obtain our preferred orientated component of bio-oil and with ease to change the contents of each component of bio-oil, the catalytic pyrolysis method was used.

Zeolites have been studied widely in the catalytic pyrolysis of biomass, and the majority of previous work was done on ZSM-5, a microporous zeolite which was

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Biographies: **Wang Shaoqing**, doctoral student, majoring in agricultural engineering, Email: wangshaoqing987@163.com; **Xu Meili**, Master, majoring in agricultural engineering, Email: xumeili000@163.com; **Wang Fang**, PhD student, majoring in agricultural engineering, Email: wangfang1987711@126.com.

***Corresponding author:** **Li Zhihe**, PhD, Professor, majoring in research of biomass energy. Shandong Research Center of Engineering and Technology for Clean Energy, Shandong University of Technology, No. 12 Zhangzhou Road, Zhangdian District, Zibo 255091, China. Email: lizhihe@sdut.edu.cn.

shown to be an effective catalyst for cracking, deoxygenation and synthesis of aromatic hydrocarbons. Li et al.^[4] found that hydrocarbons and phenols content in bio-oil increased, but the bio-oil production rate declined under HZSM-5 catalyst with different Si/Al ratios. A study about non-catalytic and catalytic rapid pyrolysis of corn stalks in a tubular fixed-bed reactor had done by Basak et al.^[5] In the catalytic process, rapid pyrolysis of stalks was executed with catalysts such as ZSM-5, HY and USY. The highest liquid yield from the catalytic pyrolysis was 27.55% with ZSM-5. Furthermore, catalytic pyrolysis converts the long chains of alkanes and alkenes into lower weight hydrocarbons, the attained oil yields were lower than those of non-catalytic pyrolysis. Moreover, Wang et al.^[6] explored the effects of two completely different catalysts, acid catalyst (MCM-41) and base catalyst (CaO), on the composition of pyrolysis vapor. They constituted that these two catalysts give different product distributions.

In order to reduce the cost of catalytic pyrolysis, a relative inexpensive and sacrificial catalyst system is essential. Red mud is a solid waste residue with strongly alkaline nature (pH>12), formed in the production of alumina^[7]. The global alumina industry produces about 90 million tons of red mud annually^[8]. As the byproduct of the Bayer process for producing pure Al₂O₃, red mud is mainly contained iron, calcium, aluminum, silicon and titanium oxides^[9]. Red Mud is always as a catalytically active material using for various substrates and reactions^[10-12]. The main reason behind using red mud is that oxides of red mud may impart synergistic effects on the overall activity. We recently manifested that red mud as an upgrading catalyst was used for catalytic pyrolysis for bio-oil preparation, as well as successfully obtained low-acidity and more stability bio-oil in a fixed-bed reactor. This study found that a co-processing of pyrolysis bio-oil with red mud and agricultural residue may deliver environmental and economical attractive synergies.

2 Experimental

2.1 Materials

The corn stalk powder used in this study was acquired

from local agricultural residues of Zibo. It was crushed and sieved to the grain of 40-60 mesh size and dried at 105°C for 24 h in an automatic drying oven. The ASTM standard test method for proximate Analysis of Corn Stalks (D 870-82) was used and ultimate analysis was carried out by an EA-3000 (EuRo Vector, Italy) elemental analyzer. Cellulose, hemicellulose and lignin are three major components which form biomass besides some extractives, ash and protein^[13,14]. The respective data are given in Table 1.

Table 1 Properties of corn stalk

Proximate analysis	wt.%
Moisture	8.42
Volatiles	67.58
Fixed carbon	14.54
Ash	9.46
HHV/MJ·kg ⁻¹	15.58
Ultimate analysis	
C	39.01
H	5.03
O	45.15
N	1.30
Other	9.51
Compositions of lignocellulosic material	
Cellulose	40.65
Lignin	4.68
Hemicellulose	28.88

2.2 Catalyst

The red mud, which was taken from Shandong Aluminium Industry Corporation China, was applied as catalyst for fast pyrolysis of biomass. It was dried at 105°C for 24 h in an automatic drying oven. Calcination was performed in muffle furnace at temperatures ranging from 200°C to 800°C for 4 h under static air after crushing the dried red mud (60-80 mesh). The energy dispersive X-ray fluorescence (EDXRF) was conducted to determine the chemical composition of dewatered red mud, by using a ZSX-100e X-ray energy spectrometer. The results are listed in Table 2, from which it can be seen that RM is composed mainly of Ca, Si, Fe, Al and Na oxides.

2.3 Apparatus

Schematic diagram of the pyrolysis experiment is shown in Figure 1. The structure contained a fixed bed reactor system, a gas condensing system and gas analysis devices. The fixed bed reactor system contained a quartz reactor with a length of 90 cm and an inner

diameter of 5 cm made of quartz glass tube, a porcelain boat, a temperature controller and an insulation device. Quartz tube reactor outlet fluid conduit is adjustable, in order to reduce the gas phase residence time for avoiding secondary pyrolysis bio-oil, while weakening condensation

wall, so as to obtain a greater yield of bio-oil. The bio-oil collection unit contained a condenser pipe filter, two collecting bottles in the ice water condenser. The non-condensable gases of passing through U dryer to gas analyzer were analyzed.

Table 2 The compositions of red mud

Component	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	TiO ₂	MgO	K ₂ O	Loss	wt. %
Content	28.64	18.35	17.97	12.72	12.14	3.15	1.25	0.64	5.14	

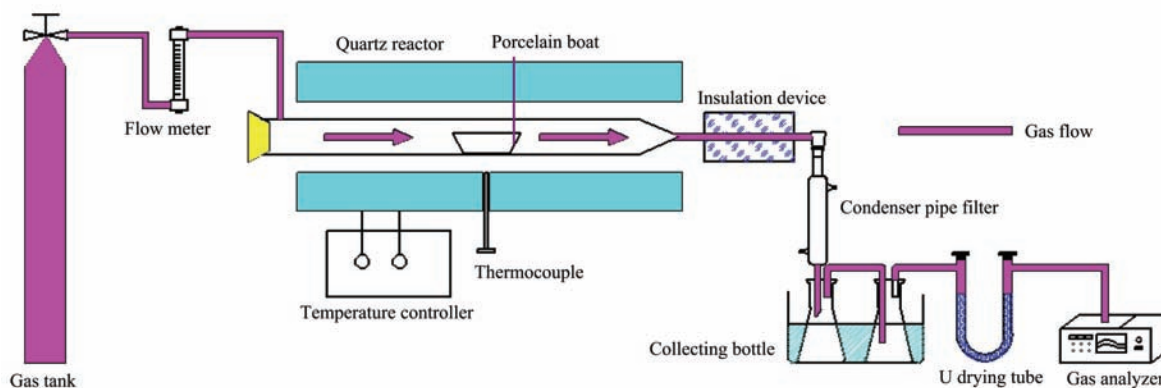


Figure 1 Scheme of biomass catalytic pyrolysis reactor system

2.4 Methods

2.4.1 Experimental procedure

Corn stalk powder was used as raw material with chosen calcined red mud as catalyst in the reaction; the content of the catalyst was 10%, 20% and 30%. The quartz reactor was heated with a heating rate of 10°C/min up to final pyrolysis temperature of 500°C, and then pushed porcelain boat with 6 g hybrid material to the reaction zone. The pyrolytic vapors were condensed into bio-oil by two-stage condensing system. The Non-condensable gas after U dryer entered the gas analyzer for analysis. After completion of the reaction, the quartz reactor held temperature of 500°C for 20 min, and then removes the porcelain boat weighed to determine the content of the char. Nitrogen was used as a carrier gas in entire pyrolysis reaction with a flow rate of 0.4 L/min. The yield of gas was calculated by the material balance. The yields (wt.%) of products were calculated as follows:

$$\text{Yields} = \frac{\text{Product}}{\text{Reaction biomass}} \times 100\% \quad (1)$$

2.4.2 Characterization methods

TGA analyses were carried out in a differential thermal balance (WCT-IC). The sample weight used

was about 10-15 mg, and the temperature ranged from room temperature to 900°C with a heating rate of 10°C/min under an air flow of 100 mL/min. X-ray powder diffraction (XRD) measurements were performed using a diffractometer (Bruker-AXS D8 Advance, Germany) with LynxEye array detector. Meanwhile, it equipped with a Madagascar optically encoded precision stepper motor. The structure was analyzed by X-ray diffraction direction and intensity. The specific surface area and pore structure of the catalysts were characterized using the series automatic surface area analyzer (Mike ASAP2020 American). It was by measuring adsorption and desorption curve of catalysts under isothermal conditions, to calculate the catalyst specific surface area and the pore structure of the surface.

The chemical composition of the bio-oil was analyzed by a gas chromatography/mass spectrometer system (Agilent 5973-6890N). Around 0.1 g of the bio-oil sample was dissolved in ethanol. For the GC separation, a capillary column DB-1701 (60 m×0.25 mm×0.25 μm inner diameter) was used. Carrier gas was helium with a flow rate of 59.7 mL/min. The column oven programme was as follows: initial temperature of 40°C with a heating rate of 5°C/min to 240°C and held during 300 s. The

mass spectrometry operating parameters: electron impact (EI) ion source at 70 eV, the scanning range of m/z 12 to 550, ion source temperature was 150°C, the interface temperature is 240°C. All data were treated by the GC/MS solution software 2.6 (Agilent, American) and the compounds were tentatively identified using the NIST-05 spectral library database^[15]. Water contents were measured by Karl-Fischer titration using a Metrohm 870 KF Titrino Plus. Heating values of the bio-oils were performed an IKA C2000 oxygen combustion bomb calorimeter. The pH measurements were determined using a PHS-2F digital pH meter (Shanghai Precision and Science Instrument Co., LTD). Gas samples were detected by an Austrian gas analyzer (Shanghai bank equipment limited company). The lower heating values (LHV) (kJ/m³) of the gas product were calculated by the following Equation (2)^[16]:

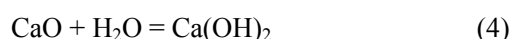
$$\text{LHV} = (30 \times \text{CO}\% + 25.7 \times \text{H}_2\% + 85.4 \times \text{CH}_4\% + 151.3 \times \text{C}_n\text{H}_m\%) \times 4.2 \quad (2)$$

3 Results and discussion

3.1 Characterization of the red mud catalyst

3.1.1 XRD analysis

After the reaction and with the removal of char, the XRD patterns of the red mud calcined at 800°C are shown in Figure 2. It is obvious from Figure 2 that is changing the laws of catalyst material composition and structure during the catalytic cracking reaction. The red mud mainly contained CaCO₃ and Fe₂O₃. The calcium carbonate diffraction peaks disappeared while ferric oxide diffraction peaks enhanced. However, new calcium carbonate diffraction peak after the reaction might be a result of some important progressive reactions as shown in Equations (3)-(5):



3.1.2 TG-DTG analysis

Thermogravimetric and derivative thermogravimetric (TG-DTG) analysis were used to explicate the effects of the calcination temperature. Figure 3 exhibits DT-DTG curves of red mud at 10°C/min. The mass deprivation of the red mud with temperature can be divided into three

steps. In the first step (<650°C), a minor mass loss (about 0.5%) was affiliated with the loss of physical absorbed water irrespective the fact of drying red mud samples at 100°C before thermogravimetric analysis. The mass loss of 10.8% of the total weight was primarily corresponding to the evaporation of chemically bound water at the temperature range of 105°C-600°C. Impurity gases and part of decomposition of carbonates induced the mass loss of 0.9% of the total weight in the range of 600°C -650°C. In the second step (700°C -750°C), the major decomposition occurred in complete decomposition of carbonates. Finally, in the third stage (>750°C), there are structural changes occurred in the solid phase of red mud. From room temperature to 900°C, the total weight loss of red mud was 17.62wt%.

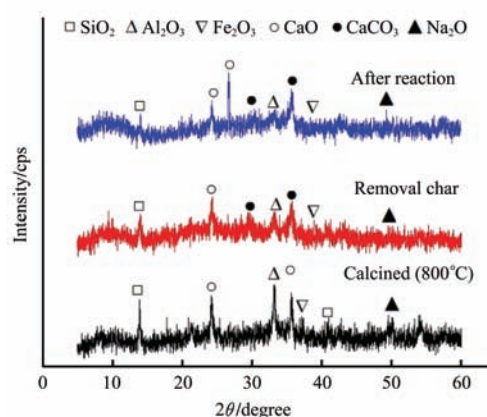


Figure 2 Powder X-ray diffraction patterns of red mud

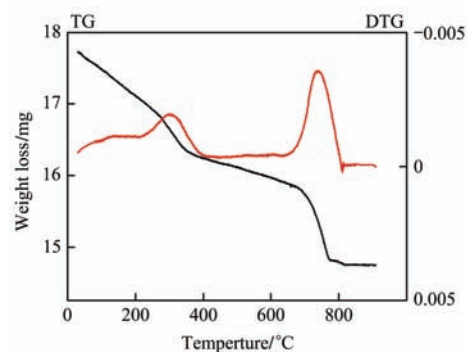


Figure 3 TG-DTG curves of red mud sample /10°C·min⁻¹

3.1.3 BET surface area and pore size

The respective data including specific surface areas, pore volume and average pore diameter are given in Table 3. These samples had a low specific surface area (18-26 m²/g), a small pore volume (0.026-0.087 cm³/g) and average pore diameter of 14-22 nm. This data bespeaked that red mud has a mesoporous nature. The red mud calcined at different temperatures could change

the surface area and pore volume greatly. The red mud possessed bigger surface area ($26 \text{ m}^2/\text{g}$) and pore volume ($0.087 \text{ m}^3/\text{g}$) at 400°C . With growing calcination temperature, specific surface area and pore volume had a corresponding diminution. The physical analysis of red mud reveals that red mud had a specific surface area and pore volume as a solid base catalyst for the catalytic pyrolysis.

Table 3 Nitrogen physisorption data of the red mud calcined at different temperature

Calcination temperature/ $^\circ\text{C}$	Surface area / $\text{m}^2\cdot\text{g}^{-1}$	Pore volume / $\text{cm}^3\cdot\text{g}^{-1}$	Average pore diameter/nm
0	22	0.064	14.23
200	21	0.063	16.59
400	26	0.087	16.48
600	19	0.073	22.04
800	18	0.026	22.15

3.2 Characterization of pyrolytic oil

3.2.1 Effects of red mud on product yields

Figure 4 depicts the effect of catalyst amount on the pyrolysis products yield. The bio-oil yield minified with cumulating the catalyst contents. Pyrolysis temperature designated in this study was more suitable for biomass fast pyrolysis, char and gas production rate is chiefly affected by the catalyst content. The gas and char yields rose with increasing the red mud summation. In pyrolysis, during deacidification reaction CO_2 content increased resulting in more gas yield. Char yield increase may be the catalyst residue after reaction.

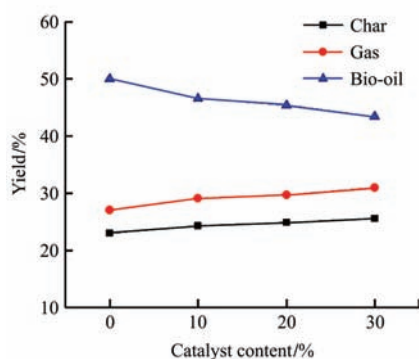


Figure 4 Effect of red mud addition on pyrolysis products yield

3.2.2 Bio-oil composition analysis

Table 4 illustrates the compositions of the bio-oil that incurred from 30% catalyst content. The peak areas do not represent the actual concentration, however indicate the pyrolytic oil component distributions. The bio-oil product is mainly dominated by oxygenated compounds.

It mainly comprised phenols, acids, alcohols, aldehydes, ketones, sugar and other substances. The phenolic compounds were dominant about 23.52%-30.85% in the pyrolytic oil. Phenols are used as an important chemical raw material which used in replacement of phenol for phenolic resins preparation^[17,18]. The ketones mainly include 1-hydroxy-2-Propanone, 1-Hydroxy-2-butanone, 3-methyl-2-Cyclopenten-1-one. Meanwhile, the bio-oil contains methyl formate, furaldehyde, furanmethanol and pyridine. Hence, the data indicated that bio-oil can be used to prepare chemicals and liquid fuels.

Table 4 GC-MS analysis results for the bio-oil obtained from 30% catalyst content

No	Name of compound	Formula	Contents/%
1	Water	H_2O	21.79
2	Methyl formate	$\text{C}_2\text{H}_4\text{O}_2$	6.71
3	2-Propanone, 1-hydroxy-	$\text{C}_3\text{H}_6\text{O}_2$	1.54
4	Pyridine	$\text{C}_5\text{H}_5\text{N}$	0.76
5	Propanoic acid	$\text{C}_3\text{H}_6\text{O}_2$	1.01
6	1-Hydroxy-2-butanone	$\text{C}_4\text{H}_8\text{O}_2$	0.88
7	3-Furaldehyde	$\text{C}_5\text{H}_4\text{O}_2$	4.13
8	2-Furanmethanol	$\text{C}_5\text{H}_6\text{O}_2$	3.00
9	3-(Diethylamino)-1,2-propanediol	$\text{C}_7\text{H}_{17}\text{NO}_2$	0.62
10	2-Cyclopenten-1-one, 2-methyl-	$\text{C}_6\text{H}_8\text{O}$	0.77
11	Ethanone, 1-(2-furanyl)-	$\text{C}_6\text{H}_6\text{O}_2$	0.56
12	1,2-Cyclopentanedione	$\text{C}_5\text{H}_6\text{O}_2$	0.79
13	2-Cyclopenten-1-one, 3-methyl-	$\text{C}_6\text{H}_8\text{O}$	1.20
14	1-Butene, 1-methoxy-	$\text{C}_5\text{H}_{10}\text{O}$	0.76
15	2(5H)-Furanone	$\text{C}_4\text{H}_4\text{O}_2$	1.37
16	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$\text{C}_6\text{H}_8\text{O}_2$	2.11
17	Phenol	$\text{C}_6\text{H}_6\text{O}$	3.94
18	Mequinol	$\text{C}_7\text{H}_8\text{O}_2$	2.83
19	Phenol, 2-methyl-	$\text{C}_7\text{H}_8\text{O}$	0.96
20	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$\text{C}_7\text{H}_{10}\text{O}_2$	0.70
21	Methyl 2-furoate	$\text{C}_6\text{H}_6\text{O}_3$	0.98
22	Phenol, 4-methyl-	$\text{C}_7\text{H}_8\text{O}$	1.39
23	Phenol, 2-methoxy-4-methyl-	$\text{C}_8\text{H}_{10}\text{O}_2$	0.74
24	Cyclopentanol	$\text{C}_5\text{H}_{10}\text{O}$	2.89
25	Phenol, 4-ethyl-	$\text{C}_8\text{H}_{10}\text{O}$	1.86
26	3-Pyridinol	$\text{C}_5\text{H}_5\text{NO}$	1.11
27	Phenol, 4-ethyl-2-methoxy-	$\text{C}_9\text{H}_{12}\text{O}_2$	0.75
28	1,4:3,6-Dianhydro- α -D-glucopyranose	$\text{C}_6\text{H}_8\text{O}_4$	1.01
29	2-Propenoic acid, 3-(2-hydroxyphenyl)-, (E)-	$\text{C}_9\text{H}_8\text{O}_3$	5.88
30	2-Methoxy-4-vinylphenol	$\text{C}_9\text{H}_{10}\text{O}_2$	3.23
31	Phenol, 2,6-dimethoxy-	$\text{C}_8\text{H}_{10}\text{O}_3$	2.62
32	Hydroquinone	$\text{C}_6\text{H}_6\text{O}_2$	0.77
33	Benzaldehyde, 3-hydroxy-4-methoxy-	$\text{C}_8\text{H}_8\text{O}_3$	0.71
34	d-Allose	$\text{C}_6\text{H}_{12}\text{O}_6$	1.04
35	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$\text{C}_{11}\text{H}_{14}\text{O}_3$	0.51
36	n-Hexadecanoic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	0.91
37	9-Octadecenoic acid, (E)-	$\text{C}_{18}\text{H}_{34}\text{O}_2$	1.99

Figure 5 shows the effect of catalyst amount for the bio-oil component distribution. The acids contents diminished significantly with increasing the catalyst contents up to 30%. The ketones and phenols enhanced

with increasing the red mud contents. The acidic contents include acetic acid, propionic acid, and cinnamic acid, the bio-oil have lower acetic acid and propionic acid after the addition of the catalyst. The reason may be acid conversion by red mud and upsurge in ketones contents might be the result of carboxylates decomposition^[19].

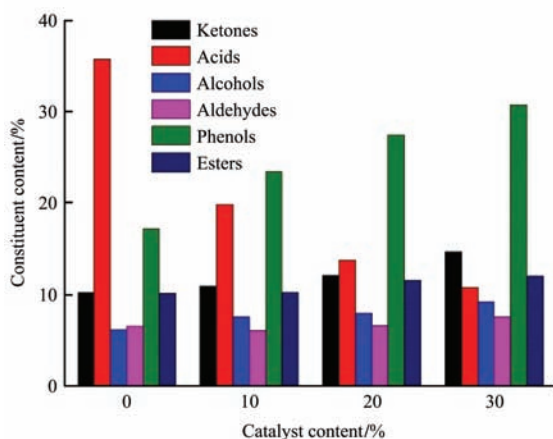


Figure 5 Constituent content contrast of the bio-oil

3.2.3 Physical properties of bio-oil

Table 5 lists the effect of red mud addition on the physical properties of bio-oil. The moisture content of the bio-oil increased significantly with catalyst addition. The higher water content of bio-oil might be likely attributed to the oxygen removal by catalytic deoxygenation converting into H_2O ^[20]. However, the calorific value of bio-oil reduced due to the increment in the moisture content. In comparison with the oxygen content of bio-oil, the increase of moisture contents was the major impact on the diminution of heating value of bio-oil. The acidity of bio-oil had greatly improved owing to the effect of red mud, the pH of bio-oil could be increased to 4.25 with catalyst content to 30%.

Table 5 Effects of red mud addition on the content of water, heating value and pH value of bio-oils

Red mud addition/%	Water content/%	Heating value/ $MJ \cdot mol^{-1}$	pH
0	26.02	17.51	2.65
10	29.25	17.23	4.13
20	32.36	16.65	4.25
30	36.59	16.32	4.32

3.2.4 Gas phase analysis

Table 6 shows the gas phase composition at different catalyst contents. Pyrolysis of lignocellulosic materials produces a gas rich in carbon oxides due to the high oxygen content of feed material^[21]. In this study, the

gas product mostly included CO_2 , CO and CH_4 . CO_2 is a product of the primary pyrolysis of cellulose and hemicelluloses^[22]. The major reason behind the increment of CO_2 in deacidification reaction during pyrolysis is red mud catalyst addition, while the largest CO_2 concentration (63.29%) was found with highest catalyst content (30%). The concentrations of CH_4 and CO are mainly affected by the secondary cracking of volatiles. As the experiment selected pyrolysis temperature ($500^\circ C$) was relatively mild, which did not intensified the secondary cracking of volatiles, thus the concentrations of CH_4 and CO changed gently. Hydrogen could not be detected due to the strong dilution with fluidizing gas (N_2). The gas product had a considerable calorific value ranging from $6.9 MJ/m^3$ to $7.8 MJ/m^3$, so it can fulfill the partial energy requirements of the pyrolysis plant.

Table 6 The gas fraction at different catalyst contents

Red mud addition/%	CO_2 /%	C_nH_m /%	O_2 /%	CO /%	CH_4 /%	H_2 /%	Calorific value/ $MJ \cdot m^{-3}$
0	58.92	1.86	1.88	30.85	4.72	1.77	7.8
10	59.36	2.24	1.93	29.72	4.86	1.89	7.4
20	61.25	2.69	1.25	28.65	4.92	1.24	7.2
30	63.29	2.72	1.05	27.32	4.02	1.60	6.9

4 Conclusions

Red mud was proved to be a basic catalyst to improve the characteristics of the bio-oil obtained from rapid pyrolysis of corn stalks. The oil yields decreased with increasing the amount of catalyst, the gas and char yields increased in the meantime. The oxygen content of bio-oil was decreased by catalytic pyrolysis because of high deoxygenation of oxygenated compounds in decarboxylation reaction, the acidity of bio-oil reduced significantly too. Removal of oxygenated component could improve bio-oil stability, storage and upgrading. The ketones and phenols increased according to the bio-oil component distribution. In order to obtain higher quality bio-oil, the study will focus on removing the moisture content in the bio-oil and improving its heating value in later experimental work. Meanwhile, the study did not conduct research on the application of the reaction residue and repeatability of catalyst performance. Overall, the co-processing of red mud and biomass was

an environmentally friendly and economical pyrolytic technical route.

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