Preparation of Dolomite-based Porous Ceramics with Al₂O₃-Loading as the Heat Carrier for Biomass Catalytic Pyrolysis

Yaya Liu, Shanjian Liu,* Weidong Liu, Dongmei Bi, and Ning Li

In biomass pyrolysis engineering, it is important to develop an industrial catalyst with efficient activity, high selectivity, and a long working life. Dolomite-based porous ceramics were considered in this work. The influence of total corn flour content on the open porosity, compressive strength, and thermal conductivity of dolomite-based porous ceramics was investigated. In order to enhance the catalytic activity, dolomite-based porous ceramics were impregnated with an $Al_2(SO_4)_3$ solution to load the Al_2O_3 catalyst. Catalytic fast pyrolysis experiments using corn stalk were conducted with the aforementioned catalyst. The bio-oil yield increased as the open porosity of the dolomite-based porous ceramics increased. The pyrolysis bio-oil yield decreased as the $Al_2(SO_4)_3$ concentration increased. The phenol content in the bio-oil increased as the Al_2O_3 load increased. Aluminum oxide not only promoted the formation of phenols in the bio-oil, but it also promoted the conversion of phenols, *e.g.*, 4-ethylphenol and 2, 6-dimethoxy-phenol. The results demonstrated that Al_2O_3 was beneficial for the formation of phenols during pyrolysis. The results detailing the preparation of Al_2O_3 loaded dolomite-based porous ceramics can provide a reference for large-scale biomass pyrolysis projects.

Keywords: Biomass; Bio-oil; Catalyst; Porous ceramics; Aluminum oxide

*Contact information: School of Agricultural Engineering and Food Science, Shandong University of Technology, Zibo 255000 China; *Corresponding author: liushanjian08@163.com*

INTRODUCTION

The overuse of fossil fuel-based energy has led to environmental pollution, *e.g.*, the greenhouse effect, acid rain, and haze (Rehman *et al*. 2019). Biomass is a renewable, abundant, and environment-friendly carbon source, which can be used as a substitute for fossil energy to produce various fuels and chemicals (Masnadi *et al*. 2014). Biomass fast pyrolysis technology is an efficient thermochemical method for converting biomass into power fuels, carbon-based materials, or high value-added chemicals (Sikarwar *et al*. 2016; Bi *et al.* 2019). In addition, some chemicals found in the bio-oil are the raw materials used to produce environment-friendly phenolic resin adhesives and bio-asphalt, *e.g.*, furfural, levulinic acid, and 5- hydroxymethylfurfural (Gao *et al*. 2018; Zhao *et al*. 2018).

It is worth noting that a suitable catalyst can play an important role during the biomass pyrolysis process, *i.e.*, decreasing the activation energy for molecular cracking reactions, or increasing the content of high-value chemicals in the bio-oil (Chen *et al*. 2017; Iliopoulou *et al*. 2018; Liu *et al*. 2019). The catalysts, *e.g.*, molecular sieve, calcined dolomite, limestone, nickel-based catalysts, zinc oxide, and aluminium oxide, have been used for biomass pyrolysis in previous studies. Among them, some rare noble metal catalysts have a higher catalytic activity, *e.g.*, nickel, platinum, palladium, barium, and

cerium, but the prices of those catalysts are high. However, coking and carbon deposition readily occur during the pyrolysis process, resulting in the deactivation of these catalysts (Kim *et al.* 2018; Hernando *et al.* 2019). In general, natural ore catalysts are not as active as noble metal catalysts during the biomass catalytic pyrolysis. However, these catalysts, *e.g.*, dolomite, limestone, kaolin, and peridot, have the advantages of low cost, abundance in nature, and are resistant to coking during pyrolysis. In addition, calcined activated dolomite or limestone have a lower mechanical strength. They are easily broken and readily form fragments, which will degrade the flow and catalytic performance of catalysts in the reactor (Montoya *et al.* 2015).

Furthermore, in biomass pyrolysis engineering, the design of the reactor and pyrolysis system also plays a key role in the generation of pyrolysis products; the design can result in the product yields and component distributions in the bio-oil greatly differing from the theoretical results. A novel V-shaped down-tube reactor, which was developed by the author's research group, has been demonstrated to be suitable for large-scale biomass fast pyrolysis (as shown in Fig.1) (Fu *et al.* 2017).
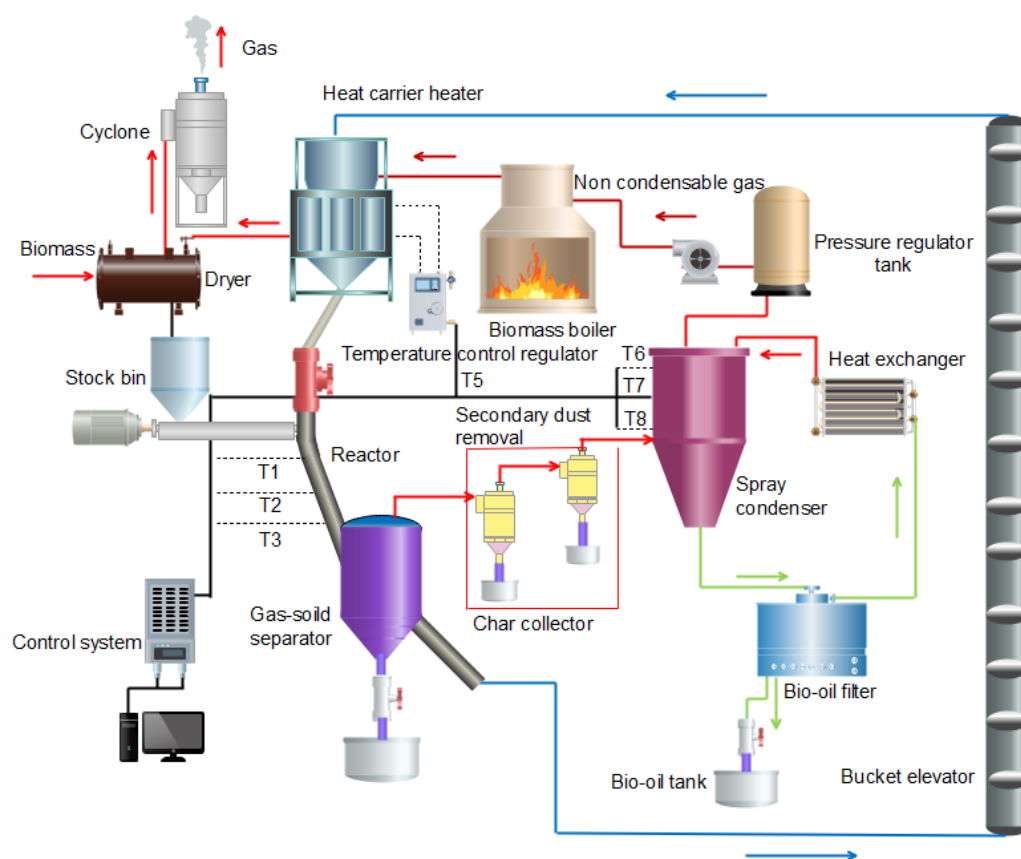

Fig. 1. Novel V-shaped down tube reactor for biomass pyrolysis

The pyrolysis reactor employs high-temperature ceramic balls, quartz sand, or metal particles as the heat carrier. Because the pyrolysis reactor does not need a large amount of carrier gas, the organic component concentrations in pyrolysis gases are high, which are easier to collect than bio-oil, causing the economic cost of the operation to be reduced. However, solid ceramic spheres with a large mass and a small specific surface area were used in previous applications, which resulted in a low catalytic capacity. The

bioresources.com

preparation of porous ceramics based on dolomite as a catalyst carrier was proposed. It is well known that porous ceramics have multiple advantages, *i.e.*, a high mechanical strength, a high temperature resistance, an anti-corrosive character, and a flexible ratio of different raw materials. Porous ceramics are used as catalysts and heat carriers in biomass catalytic pyrolysis reactors. However, the pore size distribution of porous ceramics are primarily macropores, which have the lowest "shape-selective catalysis" capacity for pyrolysis intermediate products and have weak selectivity for most target organic components in the bio-oil (Cui *et al*. 2016). In order to improve the catalytic reactivity, it has become an important concern to produce bio-oil with specific chemical components and relatively high content *via* the loading of certain metal ions on the catalyst carrier (Dai *et al*. 2020).

It should be noted that bio-oil is rich in phenols and can be extracted as a matrix for the synthesis of phenolic resin, which has good potential economic benefits (Mullen and Boateng 2011). In previous studies by the authors, it was found that the acid content decreased, while the ester and phenol content drastically increased when Al_2O_3 was used as a catalyst during biomass pyrolysis. The Al^{3+} could promote the formation of hydrocarbons, aromatics, and olefins during the catalytic pyrolysis of biomass (Zhang *et al*. 2013). Meanwhile, the Al^{3+} favoured the conversion of hydrocarbons to phenols by reducing the number of acid sites during the biomass pyrolysis process (Lu *et al*. 2018).

Since alumina is insoluble in water, it is impossible to prepare such a catalyst by impregnating alumina solution. So instead, soluble aluminum sulfate was used as the impregnant, and then the material was sintered to produce alumina and complete the loading of alumina. In this paper, the preparation of dolomite-based porous ceramics (DPCs) loaded with Al_2O_3 was introduced. The influence of the dolomite to quartz sand ratio, along with the corn flour content, on the physical properties of porous ceramics was analyzed. Furthermore, the yields of the products and the distributions of the primary components in the synthesized bio-oil under different catalytic pyrolysis conditions were studied. This paper proposed a strategy to prepare a novel and economic catalyst which favoured the production of phenols *via* biomass pyrolysis.

EXPERIMENTAL

Materials

Corn stalk was selected as the fast pyrolysis biomass material. The feedstock was pulverized and screened with a sieve size of 0.18 to 0.25 mm. The industrial analysis and elemental analysis of the corn stalks are shown in Table 1. The corn stalk was pre-dried in an electric thermostatic drying oven at a temperature of 105 °C for 24 h.

Table 1. The Proximate and Ultimate Analysis of Corn Stalk

Elemental Analysis (%)	C	H	O	N	S
	40.68 ± 2.3	6.01 ± 0.5	37.45 ± 1.5	1.44 ± 0.2	0.79 ± 0.06
Ultimate Analysis (%)	Fixed Carbon	Volatiles		Ash	Moisture
	14.54 ± 1	67.58 ± 2.8		9.46 ± 0.8	8.42 ± 0.07
Note: Oxygen content was calculated by difference					

The mineral elements of corn stalk ash were detected *via* X-ray fluorescence spectrometry (ZSX-100e, Rigaku, Japan), as shown in Table 2. The contents of the three

primary components, *i.e.*, cellulose (32.54%), hemicellulose (18.34%), and lignins (22.02%), in the corn stalks were determined using the Van Soest method (Chen *et al*. 2010).

Table 2. The Mineral Element of Corn Stalk Ash

Mineral Element	Na	Mg	Al	Si	K	Ca	Ti
Content (wt%)	0.05	3.23	0.10	12.6	9.01	5.45	0.01
Mineral Element	Cr	Mn	Fe	Ni	Cu	Zn	Sr
Content (wt%)	0.03	0.05	0.16	0.01	0.01	0.36	0.01

The Preparation of Dolomite-Based Porous Ceramics (DPCs)

DPCs can be prepared utilizing a variety of different techniques, *e.g.*, the space-holder method, foaming method, polymeric sponge dipping method, and sol-gel method (Sopyan and Kaur 2009; Sopyan *et al.* 2011; Ghomi *et al.* 2016; Moghadam *et al.* 2017). In this paper, DPCs were prepared *via* the space-holder method due to its simple processing technology. Dolomite (CaO: 30%, MgO: 22%, and CO_2: 48%) and quartz sand (SiO_2 greater than or equal to 99%) were the aggregates of the porous ceramics. In addition, corn flour and zinc borate were incorporated as the space-holder and flux of the DPCs, respectively.

The mass ratios of the dolomite and quartz sand in the aggregate of the porous ceramics were 30 to 70 and 40 to 60, respectively. The aggregate (dolomite and quartz sand) to space-holder to flux ratio was 25 to 2 to 1. The raw materials were uniformly mixed in a mixer to prepare the slurry. The slurry was rotated in a granulator, and then was sprayed with the flux to prepare the ball blank. A ball blank with diameter of 2 mm was selected to dry in an electrothermal blowing dry box until the water content was less than 15%.

The dried ball blank was placed in a cool shady spot and allowed to dry for 24 h in order to avoid cracking during the sintering of DPCs. The DPCs were sintered in a high-temperature box-type resistance furnace (SX-G08133, Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd, Tianjin, China). The sintering temperature of the porous ceramics could be decreased to 1000 °C when zinc borate (flux) was added to the paste. However, deformation and hot cracking could occur in the porous ceramics when the temperature suddenly drops during the sintering process. Therefore, the water content of the porous ceramic ball embryos was reduced to less than 15% before sintering. In the experiment, porous ceramic ball embryos with a size of 8 mesh to 10 mesh were selected.

Loading of the Al_2O_3 into the Dolomite-Based Porous Ceramics (DPCs)

In this paper, the DPCs were loaded with Al_2O_3 *via* the impregnation-calcination method. The impregnation solution was $Al_2(SO_4)_3$ at concentrations of 0.3 mol/L, 0.5 mol/L, and 1.0 mol/L. The mixture of the porous ceramic balls and $Al_2(SO_4)_3$ solution were stirred in a magnetic heating stirrer (WH240-plus, WIGGENS GmbH, Straubenhardt, Germany) at a temperature of 25 °C for 6 h. Then, the porous ceramic balls were dried at a temperature of 110 °C for 4 h. Finally, the DPCs were calcined at a temperature of 850 °C for 2 h at a heating rate of 100 °C/h. The chemical reaction of the $Al_2(SO_4)_3$ during calcination was $Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3\uparrow$. The resultant formation of the Al_2O_3 was γ-Al_2O_3 in the above reaction.

Preparation Parameters of the Dolomite-Based Porous Ceramics (DPCs)

In the reactor, the DPCs interacted with the biomass powder and reactor walls to achieve heat exchange with the biomass powder as well as catalyze the formation of pyrolysis gas during biomass pyrolysis. The porosity, bulk density, compressive strength, thermal shock resistance, thermal expansion coefficient, and thermal conductivity of the DPCs could influence the heat exchange and the catalytic activity of the catalyst.

Open Porosity and Bulk Density

The porosity of the porous ceramics consists of open porosity and closed porosity (Zou and Malzbender 2016). In this study, the DPCs were used as heat carriers and catalysts during biomass pyrolysis. Hence, the open porosity (P_a) of the DPCs was measured, as shown in Eq. 1,

$$P_a = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \tag{1}$$

as well as the bulk density (ρ), as shown in Eq. 2,

$$\rho = \frac{m_1}{m_3 - m_2} \tag{2}$$

where m_1, m_2, and m_3 are the dried mass of DPCs (g), the mass of the saturated of DPCs in the air (g), and the mass of the saturated DPCs in the water (g), respectively.

Compressive Strength, Thermal Shock Resistance, Thermal Expansion Coefficient, and Thermal Conductivity

A simple cylinder with a diameter of 20 mm and height of 20 mm was utilized to measure the compressive strength of the DPCs. The thermal shock resistance of the DPCs was measured using simple cuboids with dimensions of 120 mm × 20 mm × 10 mm. The thermal shock resistances of the DPCs were obtained at temperatures of 25, 400, and 600 °C using a thermal shock resistance tester (KRZ-S01, Guangzhou Key Instrument Co., Ltd., Guangzhou, China). Generally speaking, the thermal expansion coefficient decreased as the thermal stability increased (Roy *et al*. 1989). The test sample for measuring the thermal expansion coefficient (α) was a cylindrical porous ceramic with a diameter of 150 mm and height of 10 mm, and was calculated using Eq., 3,

$$\alpha = \frac{L_t - L_0}{L_0(t - t_0)} \tag{3}$$

where t_0, t, L_0, and L_t are the initial temperature (°C), the final temperature (°C), the length of sample at t_0 (mm), and the length at t (mm), respectively.

The thermal conductivity of the DPCs is drastically affected by the heat transfer between the biomass powder and the porous ceramic balls, the biomass powder, and the pyrolysis gas in the pyrolysis reactor. The thermal conductivity sample had a diameter of 120 mm and height of 5 mm. The thermal conductivity of the DPCs was measured with a thermal conductivity tester (THQDC-1, Xi'an Xiaxi Electronic Technology Co., Ltd., Xi'an Xi'an, China) *via* the steady state method.

Catalytic Pyrolysis Using Dolomite-Based Porous Ceramics (DPCs)

The catalytic fast pyrolysis of corn stalks was conducted using a thermostatic horizontal tube furnace reactor (SK-G06123K-3-655, Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd., Tianjin, China). The experimental system consisted of a

thermostatic horizontal tube furnace reactor and a condensation unit. First, nitrogen at a rate of 30 L/h was introduced into the experimental system for 5 min to create an oxygen-free environment. Then, the corn stalk and catalyst were mixed at a mass ratio of 1 to 5. The pyrolysis temperature was 475 °C and the pyrolysis reaction holding time was 10 min. Once the temperature of the furnace reached 475 °C, the porcelain boat serving the biomass and catalyst was quickly pushed into the reactor. The pyrolysis gas was condensed in a low-temperature thermostatic bath to obtain the bio-oil. The temperature of the condensation unit was -10 °C.

RESULTS AND DISCUSSION

The Effect of the Corn Flour Content on the Catalyst Properties

The influence of the corn flour content on the open porosity, bulk density, compressive strength, thermal shock resistance, thermal expansion coefficient, and thermal conductivity of the DPCs are shown in Fig. 2. The mass ratio of dolomite to quartz sand was 3 to 7. The mass ratio of corn flour to aggregate (dolomite and quartz sand) was 6%, 8%, 10%, and 12%, respectively.
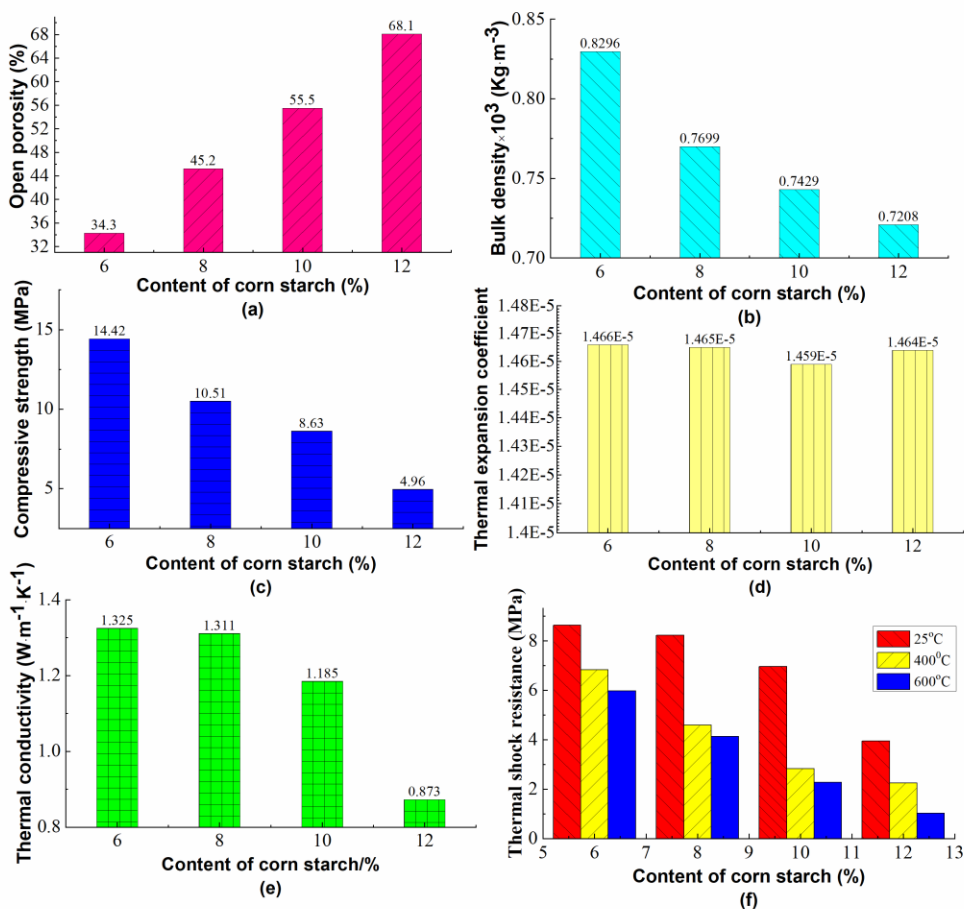

Fig. 2. The effect of corn flour content on the physical properties of the DPCs: (a) porosity, (b) bulk density, (c) compressive strength, (d) thermal expansion coefficient, (e) thermal conductivity, and (*f*) thermal shock resistance

The results showed that the open porosity of the DPCs linearly increased as the corn flour content increased. When the corn flour content was increased from 6% to 12%, the open porosity increased two-fold (Fig. 2a). The bulk density of the DPCs markedly decreased as the corn flour content increased. The bulk density decreased from 0.8296 to 0.7299 g/cm^3 when the corn flour content increased from 6% to 8% (Fig. 2b). The reason for this phenomenon was that when the corn flour content increased, the pore volume in the porous ceramics increased, thereby decreasing their bulk density. The compressive strength of the DPCs linearly decreased as the corn flour content increased. When the corn flour content increased by 2%, the compressive strength decreased by 70%. The reason for this phenomenon was that the open porosity of the DPCs was higher and the quantity of pores and voids was higher. Meanwhile, the strength of the framework in the DPCs became weaker. Thus, the compressive strength of the porous ceramics decreased as the open porosity increased (Fig. 2c). The thermal expansion coefficient of the porous ceramics did not drastically change as the corn flour content increased (Fig. 2d). The thermal conductivity of the porous ceramics decreased as the corn flour content increased. The thermal conductivity decreased by 33.4% when the corn flour content increased from 8% to 12% (Fig. 2e). The thermal shock resistance of the DPCs decreased as the corn flour content and the temperature increased (Fig. 2f).

The open porosity and compressive strength of the DPCs were high when used as a catalyst and a hot carrier during the biomass pyrolysis process. Therefore, the optimal corn flour content of the DPCs was judged to be 8%.

The Effect of the Dolomite to Quartz Sand Ratio on the Catalyst Properties

Table 3 presents the DPCs properties at different ratios of dolomite and quartz sand (30 to 70 and 40 to 60). A comparison between calcined dolomite and the DPCs clearly showed that the compressive strength was drastically improved. The reason for this phenomenon was that the CO_2 content in the dolomite was thermally decomposed, which causes the ceramic aggregate to lose weight and leave multiple irregular pores. In addition, the open porosity in sample 2 was higher than the open porosity of sample 1. Therefore, the optimum ratio of dolomite and quartz sand was 40 to 60.

Table 3. DPCs Properties at Different Ratios of Dolomite and Quartz-Sand

Number	Dolomite to Quartz Sand Ratio	Average Pore Size (μm)	Open Porosity (%)	Compressive Strength (MPa)
1	30 to 70	3.5	40.1	7.42
2	40 to 60	4.0	45.3	7.13
Note: The results in Table 3 were the average of 5 samples in each group				

The specific surface area and pore volume were detected *via* a mercury porosimeter (PoreMaster 33, Quantachrome Instruments, Boynton Beach, FL) with a ratio of dolomite to quartz sand of 40 to 60 in the DPCs. The specific surface area and pore volume of the DPCs were 0.4328 m^2/g, and 0.4329 cc/g, respectively.

Dolomite-Based Porous Ceramics (DPCs) Loaded with Al_2O_3

The loading content of Al_2O_3 crystals attached to the surface of the DPCs increased as the $Al_2(SO_4)_3$ solution concentration increased. The Al_2O_3 crystals were uniformly

dispersed on the DPCs. The loading quantity of Al_2O_3 on the DPCs was detected using an X-ray fluorescence analyzer (XRF) (XS100e 5700, RIKAGU, Tokyo, Japan), and the ratio of dolomite to quartz sand was 40 to 60 (Fig. 3).
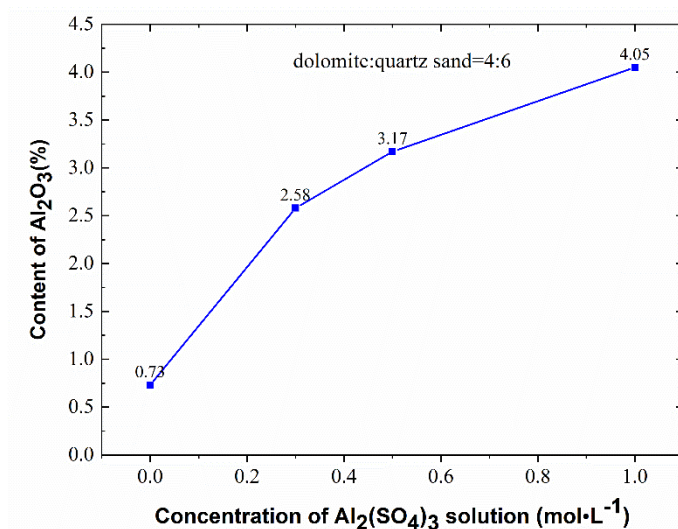

Fig. 3. The loading quantity of Al_2O_3 on the DPCs

The results showed that the loading quantity of Al_2O_3 was 2.58%, 3.17%, and 4.05% when impregnated with 0.3, 0.5, and 1 mol/L of $Al_2(SO_4)_3$, respectively. Therefore, it could be seen that loading Al_2O_3 onto the DPCs *via* the impregnation method was effective.

Dolomite-Based Porous Ceramics (DPCs) Loaded with Al₂O₃ for the Pyrolysis of Biomass

The collected bio-oil was analyzed *via* a GC/MS (Agilent 6890/5973, Agilent Technologies Inc., Santa Clara, CA) equipped with a Rtx-5 capillary column (30 m × 0.25 mm × 0.25 µm). The carrier gas was He with high purity (greater than 99.99%). The split ratio was 30 to 1, the injection volume was 0.2 µL, and the gasification temperature was 280 °C. The temperature procedure was set to increase from room temperature to 240 °C at a heating rate of 5 °C/min, and then held at 240 °C for 5 min. The ionization mode was EI and the electron bombardment energy was 70 eV. The temperature of the ion source and the interface were set at 240 and 250 °C, respectively. The non-condensable bio-gas was analyzed using an infrared gas analyzer (3100, Wuhan Sifang Photoelectric Technology Co., Ltd., Wuhan, China).

In order to determine the bio-oil (Y_o), bio-char (Y_c), and non-condensable bio-gas (Y_g) yields, the respective results were calculated according to Eqs. 4, 5, and 6,

$$Y_o = \frac{m_o}{M} \times 100\% \tag{4}$$

$$Y_C = \frac{m_C}{M} \times 100\% \tag{5}$$

$$Y_g = \frac{M - m_o - m_C}{M} \times 100\% \tag{6}$$

where m_o, m_c, and M are mass of bio-oil (g), the mass of bio-char (g), and the mass of corn stalk (g), respectively.

Table 4. Catalytic Pyrolysis Experimental Scheme

Number	Experimental Arrangement
Run 1	Pure corn stalk
Run 2	Porous ceramics (1#), corn stalk
Run 3	Porous ceramics (2#), corn stalk
Run 4	Porous ceramics impregnated with 0.3 mol/L of $Al_2(SO_4)_3$ solution (2#), corn stalk
Run 5	Porous ceramics impregnated with 0.5 mol/L of $Al_2(SO_4)_3$ solution (2#), corn stalk
Run 6	Porous ceramics impregnated with 1 mol/L of $Al_2(SO_4)_3$ solution (2#), corn stalk

The catalytic pyrolysis of corn stalk was conducted using the DPCs loaded with Al_2O_3 as the catalyst. The experimental design is shown in Table 4. The effects of the dolomite to quartz sand ratio, as well as if the DPCs were loaded with Al_2O_3, on the pyrolysis products and the distribution of the bio-oil were analyzed.
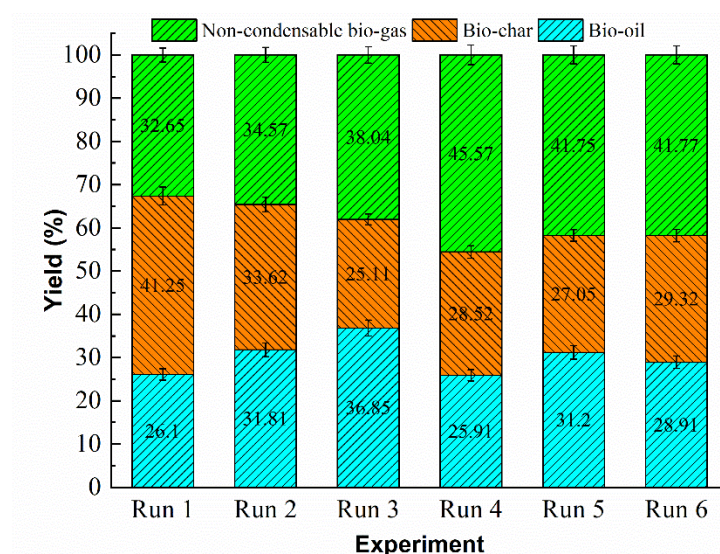

Fig. 4. The yields of the pyrolysis products from corn stalk

Figure 4 presents the yields of the pyrolysis products from corn stalk. The bio-oil yields increased as the ratio of dolomite to quartz sand increased. The bio-oil yields increased by 5.9% (Run 2), and 16.5% (Run 3) when compared with the non-catalytic pyrolysis process (Run 1). Compared with Run 1, the bio-char yields in Run 2 and Run 3 were reduced by 18.50% and 39.13%, respectively. Dolomite promoted the cracking of macromolecular organics during the biomass pyrolysis, which caused a reduction in total bio-char yield. The non-condensable bio-gas yield increased as the dolomite mass increased. A comparative analysis between Run 3 and Runs 4, 5, and 6 clearly showed that the bio-oil yield decreased when the DPCs were loaded with Al_2O_3. The addition of alumina additives may promote the conversion of other substances into phenolic substances.

It maybe breaks the bonds of the big molecules, so the coke, small molecular *e.g.* CO_2, CH_4, CO, and other non-condensable gases increased, and the output of bio-oil was reduced. The non-condensable bio-gas yields increased by 39.57% (Run 4), 27.87% (Run 5), and 27.93% (Run 6) when compared with Run 1.
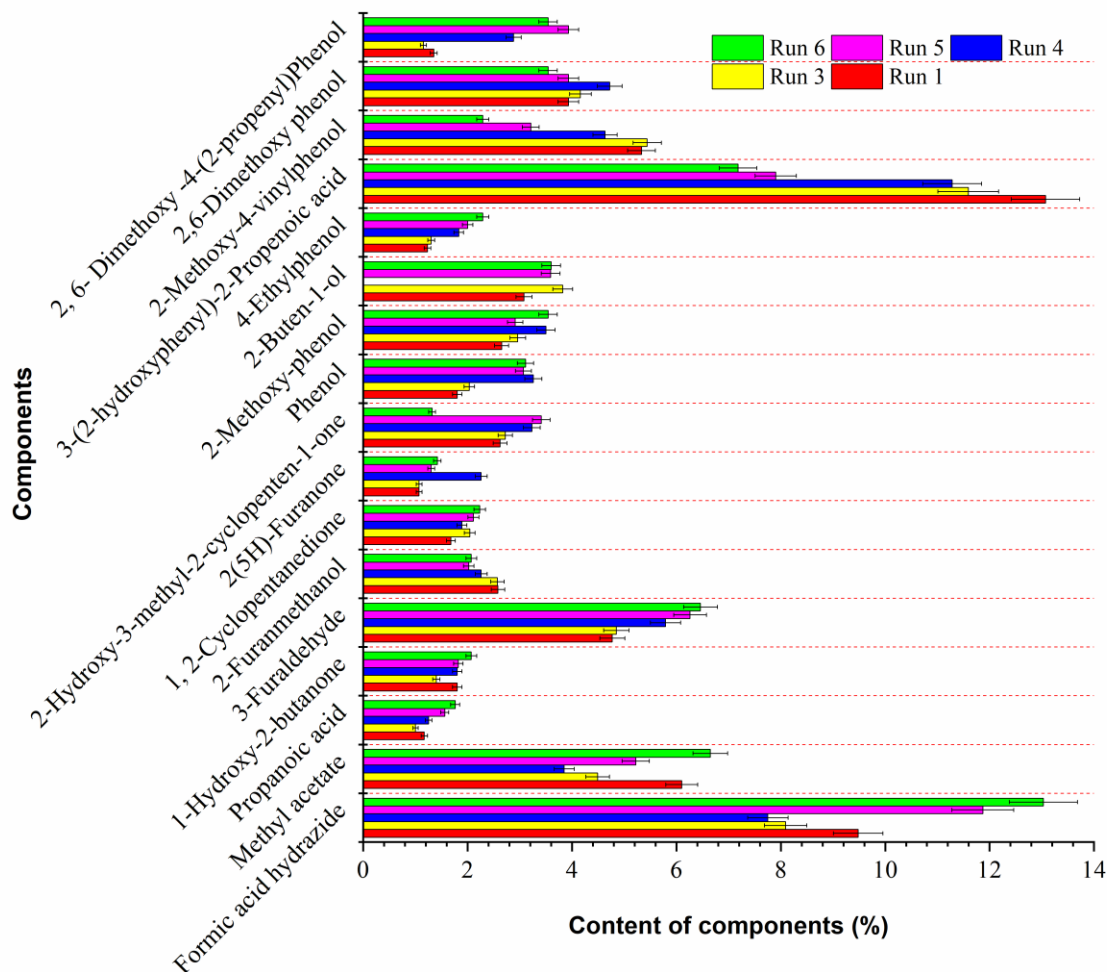

Fig. 5. Content and distribution of the components in the bio-oil

Figure 5 illustrates the chemical compounds and their distributions in the bio-oil synthesized from corn stalk. Compared with the non-catalytic pyrolysis process (Run 1), the formic acid hydrazide, methyl acetate, and 3-(2-hydroxyphenyl)-2-propenoic acid contents in the bio-oil from Run 3 decreased by 14.7%, 26.4%, and 11.3%, respectively. Meanwhile, the 3-furaldehyde and 2-methoxy-4-vinylphenol contents increased by 1.7%, and 2.0%, respectively. In order to study the influence of Al_2O_3 on the compound contents in the bio-oil, the data obtained from Runs 3 through 6 were analyzed. The formic acid hydrazide, methyl acetate, and 3-furaldehyde contents increased when Al_2O_3 was loaded on the DPCs. The formic acid hydrazide, methyl acetate, and 3-furaldehyde content increased as the Al_2O_3 loading quantity increased. The 3-(2-hydroxyphenyl)-2-propenoic acid, and 2-methoxy-4-vinylphenol contents decreased as the Al_2O_3 loading quantity increased.

There were more than 400 chemical compounds in the pyrolysis bio-oil derived

from corn stalk (Li *et al*. 2017). It was difficult to detect all the components in the bio-oil. The primary components in the bio-oil and their respective relative contents were detected *via* GC/MS and only peak areas greater than 1% were analyzed in detail.

The primary components in the bio-oil derived from Runs 1, 3, 4, 5, and 6 consisted of alcohols, ketones, phenols, acids, and aldehydes (Fig. 6).
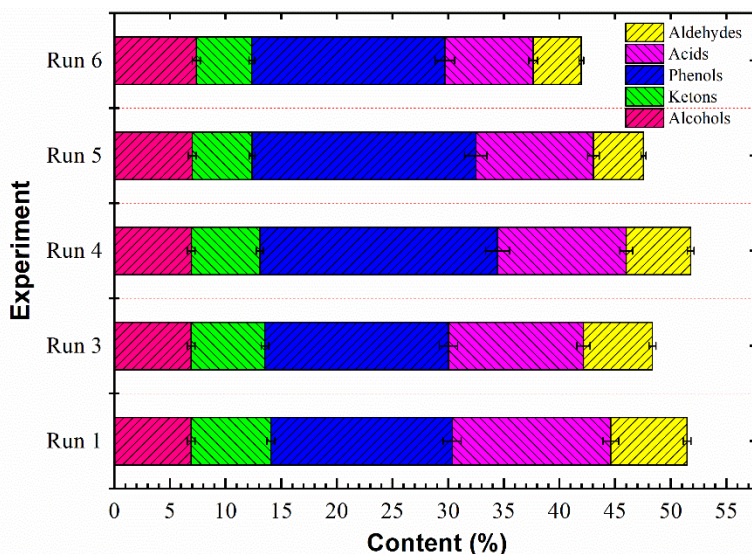

Fig. 6. Alcohol, ketone, phenol, acid, and aldehyde contents in the bio-oil

The results showed that the ketone and acid content in Run 3 were decreased by 7.5% and 14.7%, respectively, when compared to Run 1. The alcohol and phenol content in the bio-oil increased when Al_2O_3 was loaded on DPCs. The alcohol content increased while the phenol content decreased as the Al_2O_3 loading quantity increased. Therefore, the addition of Al_2O_3 can improve the cracking of macromolecules, which causes the formation of alcohols and phenols in the bio-oil during pyrolysis. The ketone content gradually decreased as the Al_2O_3-loading ratio increased. A comparison between Run 1 and Runs 4, 5, and 6 showed that the ketone content in the bio-oil decreased by 14.0%, 25.1%, and 30.5%, respectively. The ketone content in Runs 4, 5, and 6 decreased by 6.9%, 19.0%, and 24.9%, when compared to the ketone content in Run 3. This phenomenon indicated that both dolomite and Al_2O_3 promoted the decarbonylation reaction effectively, causing the removal of oxygen elements in some oxygen-containing functional groups. The phenol content in the bio-oil decreased as the Al_2O_3 loading quantity increased. The Al_2O_3 load had a complex effect on the production of phenols in the bio-oil. It not only promoted the formation of phenols, but also promoted the conversion of phenols, *e.g.*, 4-ethylphenol, 4-allyl-2, 6-dimethoxyphenol, 2-methoxy-4-vinylphenol, and 2, 6- dimethoxy-phenol. The acid content in the bio-oil drastically decreased when Al_2O_3 was loaded on the DPCs. The acid content in the bio-oil decreased by 18.8%, 25.8%, 44.4%, and 4.8%, 12.9%, and 34.6% when compared with the acid content in Run 1 and Run 3, respectively. Therefore, both dolomite and Al_2O_3 promoted the conversion of acids, which caused a reduction in bio-oil acid value.

CONCLUSIONS

1. The preparation of dolomite-based porous ceramics (DPCs) loaded with Al^{3+} *via* the space-holder method was proposed for biomass pyrolysis. The open porosity of the DPCs increased from 34.2% to 68% when the corn flour content was increased from 6% to 12%. The authors suggest that the optimal corn flour content of DPCs is 8%. This would cause the DPCs to have a higher thermal conductivity, higher compressive strength, and larger open porosity.

2. The catalytic pyrolysis of corn stalks was performed in a horizontal tube furnace reactor. The bio-oil yields increased as the dolomite content in the DPCs increased. Compared with non-catalytic pyrolysis (Run 1), the bio-oil yields increased by 5.9% (Run 2), and 16.5% (Run 3), respectively. Compared with using DPCs without the addition of a $Al_2(SO_4)_3$ solution as the catalyst (Run 3), the bio-oil yield decreased when the DPCs were loaded with Al_2O_3.

3. Compared with non-catalytic pyrolysis (Run 1), the formic acid hydrazide, methyl acetate, and 3-(2-hydroxyphenyl)-2-propenoic acid content in the bio-oil synthesized from corn stalk pyrolysis with DPCs (Run 3) decreased by 14.7%, 26.4% and 11.3%, respectively. The 3-(2-hydroxyphenyl)-2-propenoic acid and 2-methoxy-4vinylphenol content decreased as the Al_2O_3 loading quantity increased. The ketone content in the bio-oil decreased by 14.0% (Run 4), 25.1% (Run 5), and 30.5% (Run 6) when compared to Run 1. The acid content in the bio-oil was drastically reduced when Al_2O_3 was loaded on the porous ceramics.

ACKNOWLEDGEMENTS

REFERENCES CITED

Bi, D., Li, B., Liu, S., Yi, W., Jiang, M., and Lin, Z. (2019). "Influence of pyrolysis and torrefaction pretreatment temperature on the pyrolysis product distribution," *BioResources* 14(1), 1185-1197. DOI: 10.15376/biores.14.1.1185-1197

Chen, H., Ferrari, C., Angiuli, M., Yao, J., Raspi, C., and Bramanti, E. (2010). Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis. *Carbohydrate Polymers* 82(3), 772-778. DOI: 10.1016/j.carbpol.2010.05.052

Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., and Han, S. (2017). A review on the pretreatment of lignocellulose for high-value chemicals. *Fuel Processing Technology* 160, 196-206. DOI: 10.1016/j.fuproc.2016.12.007

Cui, T.-L., Ke, W.-Y., Zhang, W.-B., Wang, H.-H., Li, X.-H., and Chen, J.-S. (2016). "Encapsulating palladium nanoparticles inside mesoporous MFI zeolite nanocrystals for shape-selective catalysis," *Angewandte Chemie* 128(32), 9324-9328. DOI: 10.1002/ange.201602429

Dai, L., Wang, Y., Liu, Y., He, C., Ruan, R., Yu, Z., Jiang, L., Zeng, Z., and Wu, Q. (2020). "A review on selective production of value-added chemicals via catalytic pyrolysis of lignocellulosic biomass," *Science of The Total Environment* 749,142386. DOI:10.1016/j.scitotenv.2020.142386

Fu, P., Yi, W., Li, Z., Bai, X., and Wang, L. (2017). "Evolution of char structural features during fast pyrolysis of corn straw with solid heat carriers in a novel V-shaped down tube reactor," *Energy Conversion and Management* 149, 570-578. DOI: 10.1016/j.enconman.2017.07.068

Gao, J., Wang, H., You, Z., and Yang, X. (2018). "Gray relational entropy analysis of high temperature performance of bio-asphalt binder, its mixture," *International Journal of Pavement Research and Technology* 11(2018), 698-708. DOI: 10.1016/j.ijprt.2018.02.001

Ghomi, H., Emadi, R., and Javanmard, S. H. (2016). "Fabrication and characterization of nanostructure diopside scaffolds using the space holder method: Effect of different space holders and compaction pressures," *Material & Design* 91, 193-200. DOI: 10.1016/j.matdes.2015.11.078

Hernando, H., Ochoa-Hernández, C., Shamzhy, M., Moreno, I., Fermoso, J., Pizarro, P., Coronado, J. M., Čejka, J., and Serrano, D. P. (2019). "The crucial role of clay binders in the performance of ZSM-5 based materials for biomass catalytic pyrolysis," *Catalysis Science & Technology* 9(3), 789-802. DOI: 10.1039/C8CY02116C

Iliopoulou, E. F., Triantafyllidis, K. S., and Lappas, A. A. (2018). "Overview of catalytic upgrading of biomass pyrolysis vapors toward the production of fuels and high-value chemicals," *WIREs Energy and Environment* 8(1), 1-29. DOI: 10.1002/wene.322

Kim, H., Shafaghat, H., Kim, J., Kang, B. S., Jeon, J.-K., Jung, S.-C., Lee, I.-G., and Park, Y.-K. (2018). "Stabilization of bio-oil over a low cost dolomite catalyst," *Korean Journal of Chemical Engineering* 35, 922-925. DOI: 10.1007/s11814-018-0002-3

Li, J., Chen, Y., Yang, H., Zhu, D., Chen, X., Wang, X., and Chen, H. (2017). "Correlation of feedstock and bio-oil compounds distribution," *Energy & Fuel* 31(7), 7093-7100. DOI: 10.1021/acs.energyfuels.7b00545

Liu, Y., Nie, Y., Lu, X., Zhang, X., He, H., Pan, F., Zhou, L., Liu, X., Ji, X., and Zhang, S. J. (2019). "Cascade utilization of lignocellulosic biomass to high-value products," *Green Chemistry* 21(13), 3499-3535. DOI: 10.1039/C9GC00473D

Lu, Q., Zhou, M., Li, W., Wang, X., Cui, M., and Yang, Y. (2018). "Catalytic fast pyrolysis of biomass with noble metal-like catalysts to produce high-grade bio-oil: Analytical Py-GC/MS study," *Catalysis Today* 302, 169-179. DOI: 10.1016/j.cattod.2017.08.029

Masnadi, M. S., Habibi, R., Kopyscinski, J., Hill, J. M., Bi, X., Lim, C. J., Ellis, N., and Grace, J. R. (2014). "Fuel characterization and co-pyrolysis kinetics of biomass and fossil fuels," *Fuel*. 117(Part B), 1204-1214. DOI: 10.1016/j.fuel.2013.02.006

Moghadam, M. Z., Hassanajili, S., Esmaeilzadeh, F., Ayatollahi, M., and Ahmadi, M. (2017). "Formation of porous HPCL/LPCL/HA scaffolds with supercritical CO_2 gas foaming method," *Journal of the Mechanical Behavior of Biomedical Materials* 69, 115-127. DOI: 10.1016/j.jmbbm.2016.12.014

Montoya, J. I., Valdés, C., Chejne, F., Gómez, C. A., Blanco, A., Marrugo, G., Osorio, J., Castillo, E., Aristóbulo, E., and Acero, J. (2015). "Bio-oil production from Colombian bagasse by fast pyrolysis in a fluidized bed: An experimental study,"

Journal of Analytical and Applied Pyrolysis 112, 379-387. DOI: 10.1016/j.jaap.2014.11.007

Mullen, C. A., and Boateng, A. A. (2011). "Characterization of water insoluble solids isolated from various biomass fast pyrolysis oils," *Journal of Analytical and Applied Pyrolysis* 90(2), 197-203. DOI: 10.1016/j.jaap.2010.12.004

Rehman, A., Abdul, R., Ahmad, M., Chandio, A. A., and Deyuan, Z. (2019). "The effect of carbon dioxide emission and the consumption of electrical energy, fossil fuel energy, and renewable energy, on economic performance: Evidence from Pakistan," *Environmental Science and Pollution Research* 26, 21760-21773. DOI: 10.1007/s11356-019-05550-y

Roy, R., Agrawal, D. K., and McKinstry, H. A. (1989). "Very low thermal expansion coefficient materials," *Annual Review of Materials Science* 19, 59-81. DOI: 10.1146/ANNUREV.MS.19.080189.000423

Sikarwar, V., Zhao, M., Clough, P., Yao, J., Zhong, X., Memon, M., Shah, N., Anthony, E., and Fennell, P. (2016). "An overview of advances in biomass gasification," *Energy & Environmental Science* 9, 2927-3304. DOI: 10.1039/C6EE00935B

Sopyan, I., and Kaur, J. (2009). "Preparation and characterization of porous hydroxyapatite through polymeric sponge method," *Ceramics International* 35(8), 3161-3168. DOI: 10.1016/j.ceramint.2009.05.012

Sopyan, I., Mardziah, M., and Ramesh, S. (2011). "Fabrication of porous ceramic scaffolds via polymeric sponge method using sol-gel derived strontium doped hydroxyapatite," in: *Proceedings of the 5th Kuala Lumpur International Conference on Biomedical Engineering 2011*, 20-23 June, Kuala Lumpur, Malaysia, pp. 827-830.

Zhang, H., Xiao, R., Jin, B., Xiao, G., and Chen, R. (2013). "Biomass catalytic pyrolysis to produce olefins and aromatics with a physically mixed catalyst," *Bioresource. Technology* 140, 256-262. DOI: 10.1016/j.biortech.2013.04.094

Zhao, X., Peng, L., Wang, H., Wang, Y., and Zhang, H. (2018). "Environment-friendly urea-oxidized starch adhesive with zero formaldehyde-emission," *Carbohydrate Polymers* 181, 1112-1118. DOI: 10.1016/j.carbpol.2017.11.035

Zou, Y., and Malzbender, J. (2016). "Development and optimization of porosity measurement techniques," *Ceramics International* 42(2 Part A), 2861-2870. DOI: 10.1016/j.ceramint.2015.11.015