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The effect of industrial waste coal bottom ash as catalyst in catalytic pyrolysis of rice husk for syngas production

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ABSTRACT

Comparison between industrial waste coal bottom ash catalyst and commercial catalysts (nickel and natural zeolite) in catalytic pyrolysis of rice husk were investigated in this study. Characterization through X-ray fluorescence (XRF), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and energy disperse X-ray analysis (EDX), and *Brunauer–Emmett–Teller* analysis (BET) were carried out to understand the physiochemical activity of the catalysts in pyrolysis of rice husk. The catalyst to rice husk ratio of 0.1 was pyrolyzed in the temperature range of 323–1173 K using thermogravimetric analyzer coupled with mass spectrometer (TGA-MS) equipment to investigate the effect of catalysts in thermal degradation behavior of biomass and syngas production. The study revealed that lowest coke formation (3.65 wt%) associated with high syngas (68.3 vol%) were attained in catalytic pyrolysis using coal bottom ash catalyst compared to nickel and natural zeolite catalysts. Moreover, the hydrogen concentration had increased 8.4 vol% in catalytic pyrolysis of rice husk using coal bottom ash catalyst compared to non-catalytic pyrolysis.

1. Introduction

Environmental issues such as global warming and greenhouses gases (GHGs) have accelerated the development of renewable energy. Therefore, the government in ASEAN countries such as Malaysia has put a vast of effort in searching new alternative renewable energy. The Malaysian government has been extensively promoting the research on renewable energy in the 8–10th Malaysia Plans to increase the use of renewable energy up to 11% in the year of 2020 [1,2]. Among the renewable energy sources, biomass is considered as one of the potential candidates of the national energy matrices to reduce the reliance on fossil fuels. Biomass such as agricultural wastes [3], microalgae [4], plant residues [5] and sewage sludge [6] has attracted tremendous interest from researchers due to its renewable resource of organic carbon, abundantly available and can be converted into useful gaseous product such as hydrogen, syngas (H_2 + CO) and methane through pyrolysis process.

On the other hand, the global rice production was estimated to be 758.80 million tons in 2017 and has been acknowledged as one of the largest agriculture product in ASEAN countries. This amount could supply approximately 3.62 billion people with food and 1.45 billion people with jobs [7]. In ASEAN countries, Malaysia is one of the distinctive prominent producers of paddy. This is because rice is the staple food of all Malaysian and it played a crucial part in Malaysian diet. According to Malaysian Minister of Agriculture, the annual production of rice was estimated to be 2.8 million tons in the year of 2017 which produced approximately 0.48 million tons of rice husk (RH) on the country [8,9]. Like other lignocellulosic biomass, RH contains high amounts of organic compounds (e.g. hemicellulose, lignin and cellulose), high energy potential and high heating value which serves as the potential source for renewable energy generation [10].

Pyrolysis is one of the effective thermochemical processes to convert biomass to liquid fuel and gaseous products without the need of expensive chemical reagents. Biomass pyrolysis has vast advantages over direct combustion. It has the ability to convert low-value biomass to high quality syngas that can be used to generate electricity [11]. Recent

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Nomenclature

RH	rice husk
CP	catalytic pyrolysis
NCP	non-catalytic pyrolysis
RH/N	pyrolysis of rice husk with the presence of nickel as catalyst
RH/Z	pyrolysis of rice husk with the presence of natural zeolite as catalyst
RH/C	pyrolysis of rice husk with the presence of coal bottom ash as catalyst
TGA-MS	thermogravimetric analysis coupled with mass spectrometer
TGA	thermogravimetric analysis
DTG	derivative thermogravimetric
HHV	high heating value
WG	water gas reaction
WGS	water gas shift reaction

literature has reported that the use of catalysts during pyrolysis process can lower the energy input and time consumption as well as improve the quality of syngas compared to the conventional non-catalytic pyrolysis (NCP) [12]. Moreover, catalytic pyrolysis (CP) can significantly reduce the cost to eliminate tar in the downstream process. Apparently, a number of catalysts have been introduced into conventional pyrolysis process such as zeolites (microporous material) [13], nickel (transition metal) [14] and mesoporous material [15] to enhance the syngas production and reduce the maintenance cost of the reactor. In the last two decades, many literatures have reported on CP of RH in bio-oil production. Abu Bakar and Titiloye [16] has reported that pyrolysis process can convert RH to high quality bio-oil product using zeolite ZSM-5. Meanwhile, Balasundram et al. [12] has reported the effect of catalyst in pyrolysis of RH to obtain maximum production of bio-oil. In contrast, there were only a few papers dedicated to syngas production from CP of RH [14]. Furthermore, the high cost of these catalysts (e.g. nickel and zeolite) has limited the wide applications of biomass pyrolysis in industrial practice. From an industrial implementation point of view, the use of an expensive catalyst is not feasible because high amount of catalyst is necessary for continuous operating the process. In addition, the pyrolysis of RH process can be known as “Waste to Wealth” only if the catalyst cost is practically zero. Thus, it has a high novelty in the search of low cost catalyst for pyrolysis of RH in syngas production.

Coal bottom ash, which known as the waste product of construction industry has caused many disposal problems. Thus, it is more environmentally friendly to reduce the waste through recycling or reuse instead of landfilling. The high composition of metal oxides in coal bottom ash such as CaO, SiO, Fe_2O_3 and Al_2O_3 can serve as metal support in the catalyst. Shahbaz et al. [17] has reported that the presence of CaO in coal bottom ash can absorb the CO_2 content, resist of carbon deposition and contribute to tar elimination. In addition, it can also further enhance the production of syngas by converting the CO_2 to CO through thermal cracking process. The high content of SiO in coal bottom ash could maintain the physiochemical catalytic activity and thus, it can be easily regenerated and used as bed materials in gasification [18]. To our best knowledge, there is no well-established literature has been published about the use of coal bottom ash in pyrolysis of biomass to syngas.

Therefore, comparison between CP using commercial catalysts (nickel and natural zeolite) and industrial waste catalyst (coal bottom ash) was studied and presented in this paper. It is worthwhile to investigate thoroughly the effect of the nickel, natural zeolite, and coal bottom ash on pyrolysis of rice husk for syngas production which includes the characterization of feedstock and catalysts, the effect of catalyst in thermal degradation of rice husk, the coke formation on the catalyst in CP process and the effect of catalyst in pyrolysis process for syngas production. The experiments were performed and analyzed using thermogravimetric analyzer coupled with mass spectrometer (TGA-MS). Characterization of RH through *Brunauer–Emmett–Teller* analysis (BET), fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy disperse X-ray analysis (EDX) were investigated to understand the physiochemical properties of the RH. Meanwhile, the catalysts were characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy disperse X-ray analysis (EDX) and *Brunauer–Emmett–Teller* analysis (BET) to understand the catalytic activity in pyrolysis of RH.

2. Experimental

2.1. Biomass preparation

RH was attained from Malaysia BERNAS rice mill and used as the reference biomass in the present study. The RH was grounded and sieved to a particle size of less than 250 µm. The proximate analysis, ultimate analysis, heating values, bulk density and BET surface area of RH were presented in Table 1. The proximate analysis was conducted using thermogravimetric analyzer EXSTAR TG/DTA 6300 (Seiko Instrument Inc.) to determine the moisture, volatile matter, fixed carbon and ash content of RH. The ultimate analysis of RH was determined using LECO CHNS-932 elemental analyzer to estimate the elemental composition in RH. Furthermore, the heating value of RH was analyzed using IKA C5000 oxygen bomb calorimeter according to ASTM E711-87 method and the bulk density of RH was estimated using 100 ml Technico pycnometer at 25 °C. The surface area, pore volume and pore diameter of the RH were measured using Micromeritics ASAP 2020 surface area analyzer and porosimetry system with the standard BET equation in the relative pressure (p/p_o) range of 0.0–1.0 at the ramping rate of 10 °C/min. The functional groups of RH were evaluated in the range of 500–4000 cm^{-1} using JASCO FT-IR-4100 equipment whereas the XRD pattern of the RH was obtained using Bruker D_2 Phaser Bench

Table 1
Physical and thermochemical properties of rice husk.

Characteristic	Value	Unit
Proximate analysis[a]		
Moisture	5.56	%
Volatile matter	57.55	%
Fixed carbon	22.21	%
Ash	14.68	%
Ultimate analysis[b]		
C	38.47	%
H	5.75	%
S	< 0.01	%
N	1.68	%
O[*]	54.09	%
High heating value (HHV) [a]	15.49	MJ/kg
Bulk density[a]	172.61	kg/m^3
Particle size[a]	< 250.00	µm
BET analysis		
Surface area	1.86	m^2/g
Cumulative pore volume[c]	0.0076	cm^3/g
Average pore diameter[c]	18.25	nm

[a] Dry mass fraction basis (wt%).

[b] Dry and ash-free (wt%).

[c] BJH adsorption.

* Calculated by difference