Catalytic Pyrolysis of Coconut Shell for Bio-oil

Puttiphon Kongnum, and Sukritthira Ratanawilai

Abstract**—**Bio-oils were produced from coconut shell via fast pyrolysis process without and with HZSM-5 zeolite catalyst which carried out in a fixed-bed reactor with heating rate 30 °C/min under nitrogen atmosphere. This research was investigated the effect of pyrolysis parameters amount catalyst by a response surface methodology (RSM) experimental design. The products of pyrolysis are produced bio-oil, char and gas. The results show that flow rate of nitrogen was not significant independent variable on bio-oil product for pyrolysis. The maximum yield of bio-oil, 38.93 wt%, was obtained at temperature of 491.57 °C, particle size of coconut shell of 12.5 mm and weight of catalyst of 0.5 g with flow rate of nitrogen of 5 ml/min.

Keywords**—**biomass, pyrolysis, bio-oil, catalytic pyrolysis

I. Introduction

In this present the world is facing a serious problem on the price of fuels getting higher. This is caused by the rapid decrease in the world reserve of fossil fuels, which is using up in near future [1]. As a renewable energy source, biomass is the largest global contributor of primary energy supply, can be convent to bio-oil by pyrolysis and has some advantages compared with conventional fossil fuel [2]. In Thailand, agricultural producer is a major with abundant agricultural resources and their by product could be used as biomass energy which are characterized into processing industry (such as rice husk from the rice mill, sugarcane bagasse, palm shell, coconut shell and corn cob), is mostly used for heat and electricity for the industry, and agricultural residues (such as sugarcane tops and leaves, rice straw, soybean stalk, cassava stalk and oil palm residues).

The heating value of heat available in bio-oil is one of the most important characteristics. The standard measurement of the energy content of heating values can be reported as higher heating value (HHV) and lower heating value (LHV). The difference between HHV and LHV is equal to the heat of vaporization of water formed by combustion of the fuel [3]. Table I shown that a data for HHV of representative of biomass.

TABLE I
Higher Heating Value of Representative Types of Biomass

Biomass	HHV (MJ/kg)
Palm shell [4]	6.58
Sunflower-oil cake [5]	15.86
Rice straw [6]	16.35
Soybean cake [7]	18.17
Sugarcane bagasse [6]	18.61
Blast furnace slag [8]	19.37
Coconut shell [6]	22.83

Pyrolysis is the thermal degradation in the absence of oxidizing agent at 300 – 500 °C for converting biomass into bio-oil, gas and char. The bio-oil is liquid product from biomass by very quick exposure to heated particles in reactor. The char and gases produced are combusted to supply heat to the reactor.

Bio-oil is one of the pyrolysis products, known as pyrolysis liquid, bio-fuel-oil, pyrolysis oil, wood liquids wood oil. Generally, it is a dark-brown organic liquid and strong acrid smell [4]. The bio-oil contains more than a hundreds of organic compounds that belong to alkanes, phenols, aromatic hydrocarbon, acids, aldehydes, ketones, alcohols, esters, furans.

The catalytic hydrogenation is important to select a catalyst with higher activity. Catalytic pyrolysis derived from pyrolysis of biomass is that oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygenated groups. The zeolite catalyst, HZSM-5 has three-dimensional frameworks regular pore system that known as crystalline microporous aluminosilicates [9].

In this study, coconut shell was used to produce bio-oils based on pyrolysis process using a fixed-bed reactor amount catalyst (with HZSM-5) to optimize the bio-oil yield. The influence of several operating parameters such as temperature, flow rate of N_2, particle size of coconut shell and weight of catalyst.

II. Experimental

A. Material and sample preparation

The coconut shell sample investigated in this study has been taken from Phatthalung located in Thailand. The coconut shell was ground with a rotary grinder and sieved. Then the sample was dried in oven at 120 °C for 12 h [10].

Tsai (2006) studied the proximate and ultimate analysis of

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coconut shell. The proximate and ultimate analysis have been shown in Table II. HHV can be determined using the following as in (1). The LHV can be determined by using the HHV and weight percent of hydrogen in coconut shell according as shown in (2).

$$\mathrm{HHV\ (MJ/kg)} = \frac{338.2 \times C + 1442.8 \times (H - O/8)}{1000} \quad (1)$$

$$\mathrm{LHV\ (MJ/kg)} = \mathrm{HHV} - (0.218 \times H) \quad (2)$$

B. Catalyst preparation

The HZSM-5 catalytic was prepared by NH_4-ZSM-5. NH_4-ZSM-5 was dried in oven at 120 °C for 24 h. The dried catalytic was obtained by calcinations at 550 °C for 6 h, was conducted at nitrogen gas flow rate of 20-30 ml/min replaces the air under anaerobic condition [11].

C. Pyrolysis procedure

The pyrolysis experiments were conducted in a fixed-bed reactor (ID: 28.1 mm, length 300 mm) equipped with a sweep gas (nitrogen) connection. The reactor was heated externally stainless steel by an electric furnace and stainless steel reactor, with the temperature being controlled.

The experiments were carried out in two series. In the first part, pyrolysis without catalyst to determine the effect of reaction temperature, the effect of flow rate of N_2 and the effect of particle size. The temperature was maintained at 350-550 °C, the flow rate of N_2 was maintained at 5-15 ml/min and the particle size was maintained at 0-12.5 mm. A response surface methodology was carried out by performing 15 experiments based on a three factor. After pyrolysis the bio-oil was condensed in a series of ice condenser traps maintained the temperature between -5 to 0 °C and collected in the reagent bottles. The uncondensed gases were flared to the atmosphere. After cooling down the liquid weighted, the char product was pushed out from the reactor and collected in the char

TABLE II
PROXIMATE AND ULTIMATE ANALYSIS OF COCONUT SHELL

Characteristics	Value [6]
Proximate analysis (wt%)	
Moisture	11.26
Volatile matter	85.36
Ash	0.693
Ultimate analysis (wt%)	
Nitrogen	0.13
Carbon	51.38
Hydrogen	5.79
Sulphur	<0.01
Oxygen	30.76
HHV (MJ/kg)	20.18
LHV (MJ/kg)	18.92

collection bag and weighted. Gas weight was calculated from material balance.

The second part, which pyrolysis with HZSM-5 zeolite catalyst, was carried out to determine the effect of reaction temperature, the effect of particle size and the effect of weight of catalyst. The temperature was maintained at 450-550 °C, particle size was maintained at 6.5-15.5 mm and weight of catalyst was maintained at 0.5-4.5 g with flow rate of N_2 of 5 ml/min. The bio-oil and char products are calculated as Eq. (3) and the gas product was calculated by material balance.

$$\mathrm{yield\ (wt\%)} = \frac{\mathrm{Desired\ product\ (g)}}{\mathrm{Coconut\ shell\ (g)}} \times 100\% \quad (3)$$

D. Design of experiments

The response surface methodolygy (RSM) was developed by Box-Behnken Design (BBD). The independent variables considered were temperature (X_1), flow rate of N_2 (X_2) and particle size of coconut shell (X_3) for without catalyst and Temperature (X_4), particle size (X_5) and weight of catalyst (X_6). The low, center and high levels of each variable were designated as -1, 0 and +1 respectively as shown in Table III. In this study, the total number of experiments design was based on 3 factors and 3 levels that counted 15 runs [12].

The regression model was used to approximate the responses based on a second-order polynomial model as in (4) where Y is the response, β_0 is a constant coefficient, X are the independent variables and β_i, β_{ii} and β_{ij} are interaction coefficients of linear, quadratic and the second order terms respectively

TABLE III
EXPERIMENTAL RANGE AND LEVELS OF THE INDEPENDENT VARIABLES AMOUNT CATALYST

Variable	Pyrolysis without catalyst				Pyrolysis with catalyst			
	Code	Real values			Code	Real values		
		-1	0	+1		-1	0	+1
Temperature (°C)	X_1	350	450	550	X_4	450	500	550
Flow rate of N_2 (ml/min)	X_2	5	10	15	-	-	-	-
Particle size (mm)	X_3	6.5	9.5	12.5	X_5	9.5	12.5	15.5
Weight of catalyst (g)	-	-	-	-	X_6	0.5	2.5	4.5

TABLE IV
PARAMETER ESTIMATES AND THE STATISTICAL RESULTS OF RSM APPROXIMATION WITHOUT CATALYST

Term	Value	p-value	Summary
Constant	-34.40	0.00362	
X_1	0.146	0.00240	
X_3	8.326	3.19306e-06	$R^2 = 0.974$
X_1^2	-0.00013	0.00841	$R_{adj}^2 = 0.960$
X_2^2	0.00834	0.01064	
X_3^2	-0.388	8.33053e-06	

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 \quad (4)$$

III. RESULTS AND DISCUSSION

A. Non-catalytic pyrolysis of coconut shell

RSM based on analysis of variance (ANOVA) for significance of the regression model. It indicates that the p-value is less than 0.05 means more significant of the corresponding term of model. The p-value over 0.05 that means the model term is insignificant. The terms of model are insignificant (X_2, X_{12}, X_{13} and X_{23}) were removed from regression model. ANOVA table shows for significance of model coefficients shown in Table IV.

The maximum bio-oil yield, 52.57 wt%, was obtained as particle size of coconut shell and temperature were significant respectively. The flow rate of nitrogen was not significant independent variable on bio-oil product for pyrolysis without catalyst. So the second part, which pyrolysis by using catalytic

B. Catalytic pyrolysis of coconut shell

The catalytic pyrolysis experiments were conducted while the temperature at 450-550 °C and particle size of coconut shell at 9.5-12.5 mm with a constant sweeping gas flow rate of N_2 (5 ml/min). The results were shown in Fig. 1. The effects of temperature and particle size of coconut shell on the bio-oil yields of catalytic pyrolysis was observed that the bio-oil yields increased from 35.10 wt% to 38.93 wt% with the increasing temperature from 450 to 491.57 °C and with the particle size of coconut shell from 9.5-12.5 mm.

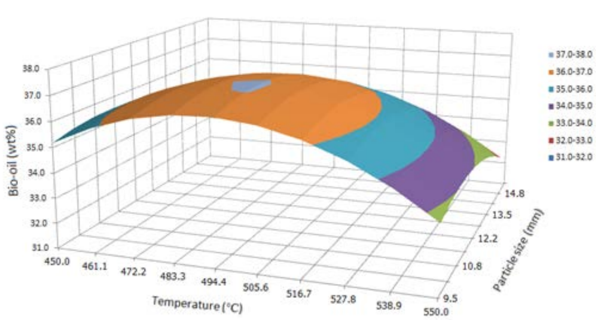

Fig. 1 Effect of temperature and particle size of coconut shell on bio-oil yield

TABLE V
PARAMETER ESTIMATES AND THE STATISTICAL RESULTS OF RSM APPROXIMATION WITH CATALYST

Term	Value	p-value	Summary
Constant	-190.53	0.00609	
X_4	0.863	0.00270	
X_5	2.828	0.07856	$R^2 = 0.863$
X_4^2	-0.000878	0.00244	$R_{adj}^2 = 0.761$
X_5^2	-0.110	0.08470	
X_6^2	0.226	0.06903	
X_5X_6	-0.136	0.01486	

The temperature was found to be the most important significant independent variable that affected the yield of bio-oil for catalytic pyrolysis that the p-value is less than others shown as table V.

IV. CONCLUSION

Bio-oils were produced from pyrolysis of coconut shell in a fixed-bed reactor by using HZSM-5 zeolite as a catalyst at different parameter such as temperature, flow rate of N_2, particle size of coconut shell and amount of catalyst. The results for pyrolysis, without catalyst show that the flow rate of N_2 was not significant. For catalytic pyrolysis, the temperature was the most significance independent variable for optimize the bio-oil yields.

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