Waste Seashell as Calcium Oxide Catalyst for Bio-oil Production From Empty Fruit Bunch

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LIST OF SYMBOLS

SYMBOLS

α	Alpha (axial distance from centre point which makes the design rotatable)
$\beta 0$	regression coefficients for the intercept coefficient
βi	regression coefficients for the linear coefficient
βii	regression coefficients for the quadratic coefficient
βij	regression coefficients for the interaction coefficient
°C	degree Celsius
σ	standard deviation
χi , χj	coded independent variables
ε	residual associated to the experiments
µm	micrometer
cc/min	cubic centimeter per minute
°C/min	degree celcius per minute
m^2 g^{-1}	meter squared per gram
cm^3/g	cubic centimeter per gram
cP	centipoise
cm^{-1}	reciprocal centimeter or wavenumber
°C/s	degree Celsius per second
ml/min	militer per minute
MJ/Kg	megajoule per kilogram
g	gram
mm	millimeter

LIST OF ABBREVIATIONS

CCD	Central Composite Design
ANOVA	Analysis of Variance
RSM	Response Surface Methodology
DoE	Design of Experiment
OFAT	One Factor At One Time
Y	Response Parameter
A	Independence variable (Particle Size)
B	Independence variable (Pyrolysis Temperature)
C	Independence variable (Nitrogen Flow Rate)
ASTM	American Standard Test Method
NIST	National Institute of Standards and Technology (NIST)
JCPDS	Joint Committee on Powder Diffraction Standards
CHNOS	Carbon Hydrogen Nitrogen Oxygen Sulfur Analyzer
TGA	Thermo Gravimetric Analysis
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared
GC-MS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
GPC	Gel Permeation Chromatography

LHV	Lower Heating Value
EFB	Empty Fruit Bunch
ZnO	Zinc Oxide
CaO	Calcium Oxide
$CaCO_3$	Calcium Carbonate
CO_2	Carbon Dioxide
CO	Carbon Monoxide
CH_4	Methane
Ca	Calcium
C	Carbon
O	Oxygen
Mg	Magnesium
K	Potassium
N	Nitrogen
PAHs	Polycyclic Aromatic Hydrocarbons
Na_2O	Sodium Oxide
TiO_2	Titanium Dioxide
Fe_2O_3	Iron (III) Oxide
CuO	Copper (II) Oxide
SrO	Strontium Oxide
RuO_2	Ruthenium (IV) Oxide
CeO_2	Cerium (IV) Oxide
Tm_2O_3	Thulium (III) Oxide
Lu_2O_3	Lutetium (III) Oxide
Co_3O_4	Cobalt (II) Dicobalt(III) Oxide

BaO	Barium Oxide
Al_2O_3	Aluminum Oxide
Cr_2O_3	Chromium (III) Oxide
H_2S	Hydrogen Sulfide
HCN	Hydrogen Cyanide

Sisa Kulit Kerang sebagai Pemangkin Kalsium Oksida untuk Penghasilan Minyak-bio daripada Tanda Kosong Buah Kelapa Sawit (TKBKS)

ABSTRAK

Sisa kelapa sawit boleh dijadikan minyak-bio melalui proses pirolisis kerana ianya merupakan sumber boleh diperbaharui bagi memastikan kesinambungan dan keupayaan untuk penyelesaian tenaga boleh diperbaharui. Ia adalah satu cabaran besar untuk menukarkan tandan kosong buah kelapa sawit (TKBKS) ke dalam bentuk produk minyak-bio dengan cara yang berkesan. Di samping itu, pemangkin digunakan dalam proses pirolisis untuk menilai kesan pemangkin dalam pirolisis proses TBKKS terhadap pengagihan minyak-bio, bioarang dan gas sebagai produk akhir yang terhasil. Oleh itu, kajian ini dijalankan untuk menilai kesan pemangkin kalsium oksida berasaskan sisa kulit kerang dengan menggunakan reaktor lapisan padat untuk penghasilan minyak-bio daripada TKBKS. Pengoptimuman parameter proses pirolisis seperti saiz zarah (A), suhu pirolisis (B) dan kadar aliran nitrogen (C) telah dikaji melalui reka bentuk komposit pusat dengan minyak-bio dianggap sebagai respon. Suhu pirolisis (B) telah dianggap sebagai parameter yang paling penting diikuti saiz darah (A). Keadaan yang optimum pada suhu pirolisis 628°C, kadar aliran nitrogen 250 ml/min dan julat saiz zarah 710-1000µm menghasilkan minyak-bio sebanyak 44.1%. Kesan pemangkin dalam proses pirolisis telah dijalankan pada keadaan optimum 5 % menghasilkan minyak-bio sebanyak 44.5%. Keputusan analisa kumpulan berfungsi menunjukkan kehadiran asid, keton, hidrokarbon aromatik polisiklik alkohol dan kumpulan karbonil. Nilai pH yang diperolehi oleh minyak-bio daripada pirolisis berpemangkin adalah lebih tinggi (pH 4.3) berbanding dengan minyak-bio daripada pirolisis tanpa pemangkin (pH 3.5). Oleh itu, keasidan minyak-bio telah dikurangkan oleh kalsium oksida pemangkin dari sisa kulit kerang. Kesan kelikatan minyak-bio diperoleh dengan menggunakan pemangkin meningkat daripada 20.5 kepada 37.8 cP. Kalsium oksida memberi kesan pada pengeluaran minyak-bio dari segi kuantiti dan kualiti. Analisa morfologi permukaan pemangkin menunjukkan kelompok kemas, bijian berliang dan permukaan seragam. Komposisi pemangkin adalah 3.0% C, 40.1% O_2 dan 56.9 % Ca. Komposisi utama pemangkin adalah kalsium oksida iaitu sebanyak 98.5%. Luas permukaan pemangkin kulit kerang terkalsin, saiz liang dan isi padu liang masing-masing adalah 10.2187m^2 g^{-1}, 122.918Å dan 0.03421cm^3 g^{-1}. Oleh itu, sisa kulit kerang yang kaya dengan elemen kalsium sesuai sebagai pemangkin yang murah dan teknologi hijau bagi penghasilan minyak-bio daripada sisa kepada kekayaan.

Waste Seahell as Calcium Oxide Catalyst for Bio-oil Production from Empty Fruit Bunch

ABSTRACT

Oil palm waste could be converted into bio-oil through pyrolytic process due to its renewable resource to ensure continuity and capacity for renewable-energy solution. It is a great challenge to convert empty fruit bunch (EFB) into liquid product which is bio-oil in an effective way. In addition, catalyst was added in the pyrolysis process to evaluate the effect of catalytic pyrolysis EFB towards the yields of bio-oil, biochar and gas as pyrolysis product yields. Therefore, this study was conducted to evaluate the effect of waste seashell based calcium oxide (CaO) as catalyst using a fixed bed reactor for bio-oil production from EFB. The optimization process parameters such as particle size (A) pyrolysis temperature (B) and nitrogen flow rate (C) were investigated through central composite design (CCD) with bio-oil considered as the response. The pyrolysis temperature (B) was considered as the most significant parameter followed by particle size (A). From the optimization study, an optimum pyrolysis temperature of 628 °C, nitrogen flow rate of 250 ml/min and the particle size of 710-1000 µm produced 44.1% of bio-oil. The functional group analysis showed the presence of acid, ketone, polycyclic aromatic hydrocarbons (PAHs), alcohol and carbonyl groups. The pH of bio-oil obtained from the catalytic process was higher than the non-catalytic process was higher than the non-catalytic process which varies from pH 3.5 to pH 4.3. Therefore the acidity of bio-oil was reduced in presence of Cao catalyst from seashell. The effect of viscosity of bio-oil obtained by catalytic process was also enhanced from 20.5 to 37.8 cP. Therefore, CaO catalyst from waste seashell affected the production of bio-oil in terms of quantity and quality. Morphological analysis of catalyst from waste seashell showed well organized, porous grains with uniform surface. The compositions of catalyst were 3.0 % C, 40.1 % O_2 and 56.9 % Ca, and total composition of the catalyst was 98.5 %. The surface area of the calcined seashell catalyst, pore size and pore volume were 10.22 m^2g^{-1}, 122.92 Å and 0.0341 cm^3g^{-1} respectively. Therefore, calcined waste seashell as calcium oxide catalyst is rich in calcium suitable as a catalyst which is very cost effective and green technology for the production of bio-oil from waste to wealth.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The global productions of biomass are enormous and different types of biomass are used all over the world for energy generation. Biomass provides a clean, renewable-energy source that could improve the environment, economy and energy security. The use of these waste materials will depend on a knowledge, economics and technologies that are used to transform them into manageable products (Sukiran, 2009) Biomass can be converted into liquid by thermochemical and biochemical techniques (Badalai & Mahanta, 2015). In biochemical technique, the biomass conversion includes metabolic action of organism or bacteria. The thermochemical conversion of biomass includes combustion, gasification, liquefaction, pyrolysis and carbonization that can be used to convert the biomass into the energy which will yield range of products such as solid, gas or liquid. Pyrolysis is a well-known technology of biomass conversion into gaseous form with application of heat in oxygen free condition. The vapour produced during pyrolysis, can be converted into liquid by condensing this vapour which is known as bio-oil. Therefore, pyrolysis of biomass has gained attention because it can produce liquid which can yield up to 75% wt. on a dry feed (Abnisa, et al., 2011). In many applications, which include boilers, furnace, engines and turbines, to generate electricity, bio-oil can be substituted as fuel oil and diesel. Besides, various chemicals such as acetic acid, food flavorings, preservatives adhesive, hydrogen and sugars can be purified using bio-oil that serve as extractant (Chan et al., 2014).

1.2 Problem Statement

Bio-oil is a key ingredient in the energy substituent and chemical feedstock but the effective use of bio-oil is restricted due to its poor quality. Bio-oil derived from pyrolysis of biomass can be highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex. The present of oxygen in the bio-oil has negative effect such as further increasing the corrosion due to its low pH. Upgrading the bio-oil by catalytic pyrolysis has received increasing consideration and the catalyst is expected to improve the yield and the quality of bio-oil. However, there are several drawbacks associated with this such as current practices which focus on the utilization of synthesized acidic or basic metal oxides. To date no work was done on utilization of waste seashell as catalyst in catalytic pyrolysis of EFB in fixed bed reactor.

1.3 Objective of the Study

The general objective of this research is to evaluate the catalytic pyrolysis of empty fruit bunch (EFB) with waste seashell in fixed bed reactor towards the distribution of product yields and composition of bio-oil obtained via non-catalytic and catalytic pyrolysis process. The specific objectives are as follows:

1. To optimize the effect of pyrolysis parameters of EFB such as pyrolysis temperature, particle size and nitrogen flow rate by central composite design (CCD) in fixed bed reactor.
2. To characterize the catalyst CaO from waste seashell and the pyrolysed bio-oil.
3. To evaluate the effect of waste seashell catalyst in the pyrolysis process.

1.4 Hypothesis

In this study, the effect of the pyrolysis parameter such as pyrolysis temperature, particle size and nitrogen flow rate on bio-oil production were investigated and then to obtain these parameters were systematically varied to maximize bio-oil yield in optimum pyrolysis condition. The waste seashell catalyst can be used in pyrolysis process as catalyst in the pyrolysis of EFB that improve towards the distribution of pyrolysis product yields. The physio chemical properties of bio-oil obtained were also evaluated.

1.5 Scope of the Study

The scope of the research is to use waste seashell as catalyst in pyrolysis process of EFB in the production of bio-oil. The surface morphological, chemical composition and surface area of the catalyst were characterized. The pyrolysis process is carried out in the fixed bed reactor. The influence of particle size, pyrolysis temperature and nitrogen sweep gas flow rate across the bed on the bio-oil yield were investigated. Design of experiment (DoE) is employed to investigate the effect of pyrolysis parameters for the production of bio-oil. A standard response surface methodology (RSM) analysis in conjunction with CCD is utilized to develop experimental runs. The optimization method of central composite design (CCD) is used to optimize the parameters (Mohamed et al., 2014). Comparative study on the effectiveness of the calcium oxide waste seashell catalyst and the commercial catalyst which zinc oxide used in bio-oil production are determined.Bio-oil is collected and analysed. Biochar produced as by-product is measured and the gas by-product is vented out as it passed through the condenser. The physical and chemical properties of the bio-oil such as viscosity, pH value, functional groups and chemical compounds of bio-oil produced are identified.

CHAPTER 2

LITERATURE REVIEW

2.1 Pyrolysis

Pyrolysis is defined as thermochemical conversion of organic material or biomass in the absence of oxygen to produce biochar, bio-oil and gas mixture (Yaman, 2004). Pyrolysis is derived from Greek words *pyro* means fire and *lysis* means decomposition or breaking down a complex mass into constituent parts at high temperature. During the pyrolysis process, complex macromolecules of biomass decompose into relatively smaller molecule producing three distinguishable products. The products are biochar comprised of carbon and ash, a mixture of gases which is mainly of carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4) and hydrogen (H_2) and bio-oil which consists of oxygenates, aromatic, water, low degree of polymerization product, and tar (Kantarelis, 2014).

Pyrolysis is an endothermic process and requires an external heat source. During pyrolysis organic compounds are distilled and vaporized to form combustible gas, by heating them in oxygen free atmosphere. The energy is necessary for driving this process, including the energy required to raise the biomass from room temperature to the reaction one (sensible energy) and the energy to convert the original biomass into the pyrolysis products (reaction enthalpy). The heat demand can be supplied by different heat sources: (i) burning an auxiliary fuel, (ii) burning the gas and/or solid fraction obtained in the process, (ii) electric heating, and (iv) hot sand or molten salts (Luo & Feng, 2017). Heat for the process can be provided by partial combustion of pyrolysis gas within the furnace and combustible elemental carbon. The oxidized portion of combustible gas may be used as fuel in external combustion chamber with resulting energy recovery by conventional waste-heat-boiler technology. Carbon levels in the furnace are higher for pyrolysis than normal incineration (Forbes et al., 2008). Waste heat is an alternative energy source for the pyrolysis processes, which facilitates energy conservation. Zhao et al., (2010) investigated that the combustible gases production from municipal solid waste using hot blast furnace slag as the heat carrier in a fixed-bed reactor.

2.1.1 Different Types of Pyrolysis

Pyrolysis can divided into three main categories which are differentiated by pyrolysis temperature, heating rate, solid residence time and biomass particle size. The three types of pyrolysis are slow pyrolysis, fast pyrolysis and flash pyrolysis. The processes vary from each other in term of chemistry, overall products and quality of yields (Jahirul, et al., 2012).

Slow pyrolysis is generally conducted to enhance biochar and syngas production at low temperature with a low heating rate at 0.1-1°C/s. In contrast, the fast pyrolysis generally used for production of bio-oil at high heating rate between 10-200°C/s. This process or condition will generate high yield of bio-oil production and a small amount of biochar. As for flash pyrolysis, it needs a high heating rate of more than 1000°C/s, a very short residence time and small of particle size which is less than 0.2 mm in order to reduce internal heat transfer limitation (Marshall, 2013). Table 2.1 represents the summary of types of pyrolysis.