Characterization of lignocellulosic biomass thermal degradation and physiochemical structure: Effects of demineralization by diverse acid solutions

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A B S T R A C T

To eliminate the negative impacts of inorganic constituents during biomass thermochemical processes, leaching method by different diluted acid solutions was chosen. The different palm oil biomass samples (palm kernel shell (PKS), empty fruit bunches (EFB) and palm mesocarp fiber (PMF)) were pretreated by various diluted acid solutions (H_2SO_4, $HClO_4$, HF, HNO_3, HCl). Acids with the highest degrees of demineralization were selected to investigate the dematerialization impacts on the biomass thermal characteristics and physiochemical structure. Thermogravimetric analysis coupled with mass spectroscopy (TGA-MS) and Fourier transform infrared spectroscopy (TGA-FTIR) were employed to examine the biomass thermal degradation. TGA and DTG (Derivative thermogravimetry) indicated that the maximum degradation temperatures increased after acid pretreatment due to the minerals catalytic effects. The main permanent evolved gases comprising H_2, CO_2, CO were detected online during analysis. The major permanent gases produced at the temperature range of 250–750 °C were attributed to the condensable vapors cracking and probably some secondary reactions. The physiochemical structure change of the acid-treated biomass samples was examined by using Brunauer Emmett Teller (BET) method, Scanning Electron Microscope (SEM) and FTIR. The pyrolysis kinetics of the different palm oil biomasses were investigated using first order reaction model.

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1. Introduction

Depletion of fossil fuel resources and environmental issues associated with the CO_2 accumulations in the atmosphere are the main reasons increasing the attentions toward renewable energy resources like biomass.

Various thermochemical technologies (pyrolysis, torrefaction, gasification, etc.) can be utilized to convert the biomass to the bio-oil. Among them, pyrolysis is a remarkable and most known industrial technology used for the bio-oil production. Pyrolysis can be defined as the conversion of the biomass to liquid bio-oil, solid charcoal and gaseous products in the absence of oxygen under atmospheric pressure and moderate temperature ranging from 300 to 600 °C [1]. The major constituents of the biomass are cellulose, hemicelluloses, lignin, inorganic and some extractives, which have different thermal behavior during pyrolysis [2,3].

Thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) have been utilized by different researchers to investigate the biomass pyrolytic behavior and kinetics [3–7]. TGA coupled with mass spectrometry (MS) and infrared spectroscopy (FTIR) provides the conditions for real-time (online) quantitative and qualitative evolved gas analysis, respectively. The utilization of MS and FTIR techniques along with thermal analysis can facilitate a deeper insight of the kinetic scheme and consequently to understanding the actual reaction mechanism [8,9]. Several investigations on the biomass thermal analysis have been carried out using integrated TGA-MS [10–12].

The effects of inorganic metals on thermal degradation of the lignocellulosic biomass have been intensively studied by researchers [13–17]. They mostly concluded that, the presence of alkaline and alkaline earth metallic species (K, Na, Mg, and Ca) can influence the quality and quantity of the pyrolysis and gasification products. Commonly, inorganic species are maintained on the char

surface instead of being volatized during pyrolysis process. Therefore, they can catalyze the biomass conversion and char formation reaction [18,19]. The high inorganic constituents in the bio-oil, originated from the biomass having high quantity of minerals, can catalyze polymerization reaction during the bio-oil storage and led to its viscosity increase [20], whereas their removal from the biomass before pyrolysis can increase the bio-oil yield and stability [21].

Biomass demineralization with acid solutions had been indicated to be a suitable method to remove inorganic constituents from the biomass, and to improve its fuel properties. So, various leaching experiments using diverse conventional acid solutions including hydrochloric acid, sulfuric acid, hydrofluoric acid, perchloric acid, nitric acid et al. were conducted [17,19,22–24].

Biomass pretreatment using acid solution before pyrolysis can eliminate the needs for additional fractionation step. This advantage can facilitate a considerable simplification of the process and large scale bio-oil production, as well as extensive reduction of energy consumption and cost of pyrolysis [24]. Furthermore, minerals elimination from the used acid solution (recovery) and its recycling to the pretreatment stage can enhance process economy and make it environment-friendly.

TGA/DTG investigations carried out by Müller-Hagedorn et al. [25] showed the doped biomass with inorganic spices (Na, K and Ca) shifted DTG curves to lower temperature compared with washed and untreated biomass. Further, it was proved that the doped biomass with potassium decreased activation energy compared to that of washed one [26]. As mentioned, several researches available in the literatures have focused on the effects of inorganics on the biomass behavior, but only a few investigations on the leaching process effects on the biomass physiochemical structure [17,23] have been reported. To the best of our knowledge, no published study has been reported on the effects of minerals removal (using acid solutions) on the palm oil biomasses thermal degradation and physiochemical structure.

This study is aiming to find the most efficient acid solutions to leach out the minerals from the biomass samples and to investigate the impacts of these diluted acids on the physiochemical structure and thermal behavior of the palm oil biomasses. In this regard, the different palm oil biomass samples (PKS, EFB and PMF) were pretreated by H_2SO_4, $HClO_4$, HF, HNO_3 and HCl diluted solutions to remove inorganic species through leaching process. Consequently, the treated samples with the highest degree of ash removal were profoundly analyzed to measure the demineralization efficiency and the effects of deashing process on the thermal degradation and the physiochemical structure of the biomasses. TGA-MS and TGA-FTIR were employed to study the pyrolysis characteristics, evolved permanent gases products distribution and reaction kinetics.

2. Materials and methods

2.1. Biomass materials

The palm oil biomasses comprising palm kernel shell (PKS), empty fruit bunches (EFB) and palm mesocarp fiber (PMF) were obtained from Szetech Engineering Sdn. Bhd. located in Selangor, Malaysia. The samples were crushed using high-speed rotary cutting mill and sieved to desired particle size (<300 μm). Then, the samples were dried at 105 °C for 24 h and kept in tightly screw cap plastic bottles.

2.2. Demineralization pretreatments

Different types of the dried palm oil biomasses (PKS, EFB and PMF) were subjected to diverse diluted acid solutions (H_2SO_4

(96 wt.%), $HClO_4$(70 wt.%), HF(49 wt.%), HNO_3(65 wt.%), HCl (37 wt.%)), all supplied by R&M Chemicals, for the purpose of inorganics removal. Acid washing pretreatment process aimed to maximize the ash extraction through leaching process. For this purpose, 20 g of the biomass samples were treated by 2.0 M acid solutions at room temperature for 48 h and then filtered and washed with distilled water. The ratio of the acid solutions to the biomass samples was considered as 15 (g solution/g biomass). The washing process was continued to a constant pH value. The leached biomass samples were dried in oven at 105 °C over 24 h and kept in tightly screw cap bottles.

2.3. Biomasses proximate and ultimate analysis

Proximate analysis was carried out by utilizing thermogravimetric analysis. Volatile matter, fixed carbon and moisture contents were measured according to ASTM D-5142-02a using TGA/ Q500 manufactured by TA Instruments. Ash content of the biomasses samples was determined by their ignition in a muffle furnace at 575 °C for 24 h according to ASTM E-1755-01 standard method. Ash content (wt.%) was calculated by dividing ash weight to initial weight of dried biomass sample at 105 °C.

Ultimate analysis was carried out to determine the basic elemental composition of the biomass samples. The samples' ultimate analysis was done using a Perkin–Elmer model 2400, Series II CHNS/O analyzer to measure carbon, hydrogen, nitrogen and sulfur contents. Oxygen content was then calculated by difference. Higher heating value (HHV) was calculated from the elemental compositions using Eq. (1) from Channiwala and Parikh [27]:

$$HHV\left(\frac{MJ}{kg}\right) = 0.3491C + 1.1783H + 0.1005S - 0.10340$$
$$- 0.0151N - 0.0211A \quad (1)$$

where C, H, N, O, S and A represents carbon, hydrogen, nitrogen, oxygen, sulfur and ash contents of materials, respectively, expressed in dry basis weight percentage.

2.4. X-ray Flouresence (XRF) analysis

All the biomass samples inorganic contents were quantified using X-ray Flouresence (XRF) instrument (PANalytical Axios^{mAX}).

2.5. Scanning Electron Microscopy (SEM) analysis

The surface nature of the virgin and treated samples was investigated by SEM (model FEI QUANTA 450 FEG, operating at a 5 kV accelerating voltage and low vacuum) to characterize the effects of leaching process on the physical structure of the biomasses. Conductive coating was not applied to prepare the samples for SEM analysis. Samples were prepared by their sticking on carbon sheet.

2.6. Surface area and porosity analysis

The surface area and pore size of the samples were measured, using nitrogen (N_2) adsorption/ desorption isotherm at −196 °C, by the Micrometrics ASAP 2020 gas adsorption analyzer. All the samples were degassed in vacuum at 130 °C for 24 h before the measurement. Filler rod was used in the sample tube due to low surface area of samples. Estimation of pore size diameter was done by Barrett–Joyner–Halenda (BJH) method.

2.7. FTIR spectroscopy

To qualitatively analyze the functional groups of chemical components available in the virgin and pretreated biomass samples,