In-depth investigation on thermochemical characteristics of palm oil biomasses as potential biofuel sources

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ABSTRACT

The accurate determination of the biomass thermal properties is particularly important while studying biomass pyrolysis processes. The aim of this study is to investigate the different palm oil biomass samples (palm kernel shell (PKS), empty fruit bunches (EFB) and palm mesocarp fiber (PMF)) thermochemical behavior during pyrolysis. Thermogravimetric analysis coupled with spectroscopy (mass spectroscopy (TGA-MS) and Fourier transform infrared spectroscopy (TGA-FTIR)) and also differential scanning calorimetry (DSC) were employed to investigate the biomass thermal degradation. TGA and DSC results were obtained at temperature ranging from 25 °C to 850 °C and 500 °C, respectively, using pure nitrogen as inert gas and at the heating rate of 15 °C/min. TGA curves showed different stages for the biomasses thermochemical behavior associated with dehydration (stage 1), slow depolymerization (stage 2) and pyrolytic degradation (stage 3), while DSC indicated the caloric requirement in these stages. 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 biomasses pyrolysis, oxygenated functional groups cleavage and probably some secondary reactions. Furthermore, the bio-oils produced from the different biomasses pyrolysis, in a fixed-bed reactor, were analyzed by GC–MS and FTIR. The pyrolysis kinetics of different palm oil biomasses were investigated using the Coats-Redfern model.

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1. Introduction

The attentions toward producing energy from energy resources like biomass has increased in the past few decades, owing to depletion of fossil fuel resources and environmental issues associated with the carbon dioxide accumulations in the atmosphere. Bio-oil, which is derived from biomass, can be an eligible substitute for the fossil fuels [1–4].

Malaysia, as the largest producer and exporter of palm oil, has a great potential for the exploitation of oil palm biomasses as a source of renewable energy. Different palm oil producers in Malaysia produce substantial volume of lignicellulosic waste materials in the form of palm kernel shell (PKS), empty fruit bunches (EFB) and palm mesocarp fiber (PMF) [5].

Various thermochemical technologies (pyrolysis, torrefaction, gasification, etc.) can be utilized to convert the biomass to the energy. 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 [6–8]. The major constituents of the biomass comprising cellulose, hemicelluloses, lignin, inorganic and some extractives have different thermal behavior during pyrolysis [6,9–12].

Thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) have been utilized to investigate the biomass pyrolytic behavior and kinetics by different researchers [13–19]. TGA coupled with mass spectrometry (MS) and infrared spectroscopy (FTIR) provides the conditions for real-time (online) quantitative and qualitative evolved gas analysis. 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 [20–24]. Several investigations on the biomass thermal analysis have been carried out using integrated TGA-MS [22,25–27].

Differential scanning calorimetry or DSC is a thermoanalytical technique to investigate the caloric requirement of the biomass pyrolysis. By analyzing DSC curve, the calorimetric characteristic under different conditions can be investigated. Thus, corresponding

caloric requirements can be quantified, and the relationship of the caloric requirements with the temperature can be studied. DSC proved to be an effective technique for obtaining reliable values of the heat of reaction [28].

Knowledge of the biomass chemical composition, reactivity and thermal behavior are crucial for the efficient operation and design of thermochemical process units [29]. In this regard, thermoanalytical analysis, such as thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), provide these information in a straightforward approach [30,31]. TG analyses are based on the volatilization rate of the sample, which is dependent on the type and heating rate applied to the sample. In contrast, DSC is based on measurements of the sample energy change under a programmed heat cycle. To the best of our knowledge, no published comprehensive study has been reported on the thermochemical characteristics of the palm oil biomass samples.

In this work, the thermal behavior of the palm oil biomasses (PKS, EFB and PMF) during pyrolysis of the biomasses were investigated and characterized. Thermogravimetric analysis coupled with mass spectroscopy (TGA-MS), FTIR (TGA-FTIR) and differential scanning calorimetry (DSC) were employed to study the pyrolysis characteristics, evolved permanent gases products distribution and pyrolysis kinetics. A fixed bed reactor was designed and fabricated to carry out the biomass samples pyrolysis. The produced pyrolysis vapors after passing through the reactor were quenched by two condensers and formed liquid bio-oil. GC–MS and FTIR were employed to analyze the yielded pyrolysis bio-oils.

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. Biomasses proximate and ultimate analysis

Proximate analysis was carried out utilizing thermogravimetric analysis. Volatile matter, fixed carbon and ash 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.

Ultimate analysis was carried out to determine the basic elemental composition of the biomasses 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. All the biomasses inorganic contents were analyzed using X-Ray Flouresence (XRF) instrument (PANalytical Axios ^{mAX}). Higher heating value (HHV) was calculated from the elemental compositions using below correlations from Channiwala & Parikh [32,33]:

$$HHV \left(\frac{MJ}{kg} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O$$
$$- 0.0151N - 0.0211A \tag{1}$$

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.

2.3. FTIR spectroscopy

To qualitatively analyze the functional groups of chemical components available in the biomass samples and yielded bio-oils, Fourier transform infrared spectroscopy (FTIR; model: BRUKER TENSOR 27) was utilized. The samples were scanned over the range from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. TGA-MS and TGA-FTIR experiments

TGA (TA Instruments Q500) coupled with mass spectrometer (PFEIFFER Vacuum-Thermostar^{TM}) and TGA (NETZSCH STA 449/F3) linked with infrared spectrometer (BRUKER TGA-IR) were utilized to analyze the biomasses thermal behavior and detect the released gases simultaneously.

All experiments used pure nitrogen (99.999%) as carrier gas. To avoid condensation of heavy evolved gas components, a skimmer coupling system was employed in each instrument while the connection capillary tubes between TGA instruments and released gas analyzers (MS and FTIR) were kept at 200 °C.

To prevent mass and heat transfer effects limitations during the biomasses analysis, experiments were carried out under pure nitrogen flow rate of 150 ml/min and quantity of the samples was chosen approximately 5 mg having particle size less than 300 μm.

FTIR online gas analysis was recorded from 4000 to 400 cm^{-1}. Mass spectrometer worked with electron ionization energy of 70 eV and provided mass spectra up to 300 a.m.u. MS spectra corresponded to 2, 28, 44 a.m.u. indicated the release of main pyrolysis gases H_2, CO, and CO_2, respectively [34].

2.5. DSC analysis

Differential scanning calorimetry (DSC) was employed to compute the energy required to thermally decompose palm oil biomasses. The DSC (Model DSC1/500, METTLER TOLEDO) with refrigerated cooling system operated under nitrogen atmosphere at a flow rate of 20 ml/min. Approximately 5 mg samples were heated at heating rate of 15 °C/min from 25 °C to 500 °C using aluminum sealed pan with a pinhole in the lid to enable removal of adsorbed water and released gases during analysis. Heat flow (mW), temperature (°C) and time (min) were all recorded during analysis. The equipment was calibrated before use according to manufacturer's specifications.

2.6. Biomass pyrolysis reaction kinetics

The solid state pyrolysis kinetics of biomass using different models have been investigated by several researchers [35]. Eq. (2) shows the general reaction rate equation as:

$$\frac{dx}{dt} = kf(x) \tag{2}$$

where x is the conversion degree of the biomass feedstock expressed in Eq. (3), k is the reaction rate constant and $f(x)$ refers to a selected model of reaction mechanism.

$$x = \frac{m_0 - m_t}{m_0 - m_f} \tag{3}$$

where m_t is corresponded to the sample mass at time t, m_0 and m_f are initial and final mass of biomass, respectively. The reaction rate constant can be obtained from Arrhenius equation as:

$$k = k_0 \exp \left(\frac{-E_a}{RT} \right) \tag{4}$$

where k_0 is rate constant pre-exponential factor, E_a, R and T are activation energy (Kj/mol), universal gas constant (8.314 J/mol K),