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Research paper

Extraction of palm kernel shell derived pyrolysis oil by supercritical carbon dioxide: Evaluation and modeling of phenol solubility

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ABSTRACT

The extraction and recovery of value-added chemical compounds, such as phenolic compounds present in bio-oil has been a vital subject of study recently. In this work, the extraction of bio-oil using supercritical carbon dioxide (sc-CO_2) with particular interest in apparent solubility of phenol (a major chemical compound in pyrolysis oil) was evaluated at various temperatures (50, 60 and 70 °C) and pressures (30, 35 and 40 MPa). Highest extraction yield of bio-oil was obtained at 70 °C and 40 MPa. The phenol content in the extracted bio-oils were also studied and reported. As a preliminary study, the apparent solubility data of phenol in sc-CO_2 was successfully modeled using the values from the correlation of Chrastil, Adachi & Lu and Bartle models. The model parameters for these equations were determined and reported in this work. It was found that Chrastil, Adachi & Lu and Bartle models produced satisfactory correlations on the solubility of phenol in sc-CO_2, with AARD values of 1.51%, 6.52% and 1.85%, respectively.

1. Introduction

With increasing concerns for the search of green alternatives to relief our heavy dependency on non-renewable fossil-based resources, bio-oil (liquid product) production from various biomass feedstocks via pyrolysis or liquefaction has received considerable attention [1]. In pyrolysis, biomass is decomposed and degraded by heat at high temperatures (> 400 °C) in the absence of oxygen to produce condensable pyrolysis vapor (bio-oil), incondensable gases and solid char [2]. In liquefaction, the complex matrix structure of biomass is broken down solvolytically by heated and pressurized solvent, producing liquid products which are extracted using various organic solvents as bio-oil [3]. As a complex mixture of organic compounds, bio-oil constitutes various oxygenated compounds, such as phenolic compounds, alcohols, carboxylic acids, ketones, aldehydes and polyaromatic hydrocarbons [4]. These oxygenated compounds result in several undesirable properties in bio-oil, which include high instability under storage and heating conditions, high water and oxygen contents, high viscosity and corrosiveness, and low miscibility with conventional petrofuels [5]. Hence, the limitation of direct utilization of crude bio-oil efficiently in various applications signifies that bio-oil needs to be upgraded or refined prior to further use as biofuels or value-added fine chemicals.

Extraction and recovery of valuable chemicals from bio-oil have been extensively investigated by researchers as one of the downstream processing methods for bio-oils [6]. In this context, various techniques which include temperature-swing extraction [7], liquid-liquid extraction (LLE) by organic solvents [8], ionic liquids extraction [9], aqueous extraction [10], fractionation by phase separation [11] and steam distillation [12] have been reported in the literature. However, these reported extraction techniques posed some drawbacks including toxicity of organic solvents used, long extraction time, high process energy requirement, contamination of extracts and degradation or chemical alteration of thermal sensitive chemicals. Hence, supercritical fluid extraction (SFE), in which supercritical carbon dioxide (sc-CO_2) is

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commonly used as the solvent, is a promising alternative for extraction of chemicals/substances due to its innocuousness, low critical parameters, recyclable and cheap, relatively inert and easy separation from the extracts [13].

Phenol is amongst the major constituents of bio-oil derived from catalytic fast and intermediate pyrolysis of lignocellulosic biomass, as a degradation product of lignin present in the feedstocks [14]. In this regard, palm kernel shell (PKS) is an attractive candidate for conversion to phenolic-rich bio-oil due to its high lignin content [15]. As phenol is a valuable chemical used in a wide range of industrial applications: production of phenol formaldehyde resins, antioxidants, gasoline additives, synthesis of pharmaceuticals, precursors for polymerization, and pesticides [16,17], its efficient recovery from bio-oil is worth to be studied. Extraction of phenol from bio-oil has been reported in several studies using various techniques. Patel et al. [18] optimized the extraction of cardanol and phenol from bio-oils obtained through vacuum pyrolysis of cashew nut shells and sugarcane bagasse using sc-CO_2. Fu et al. [19] studied the extraction of phenols from pyrolysis oil using switchable hydrophilicity solvent (SHS) and up to ~70% of phenolic compounds were recovered in the extracts. Wang et al. [20] reported a new method of reactive extraction forming intermediate complexes to recover phenolic compounds from bio-oils. Yang et al. [21] performed the separation of phenols and ketones from bio-oil using extraction-column chromatography and obtained good recovery of phenols.

The solubility of a solute in supercritical fluid medium is an important subject, in which design and optimization of SFE processes can be carried out successfully on the basis of solubility data [22]. However, due to the wide spectrum of chemical compounds present in bio-oils, few experimental studies regarding SFE of actual bio-oil were reported. The lack of actual vapor-liquid equilibrium (VLE) data for multi-component system (bio-oil) remains the current challenge for process design of bio-oil fractionation. In this work, the extraction of bio-oil by sc-CO_2 and evaluation of phenol solubility at various temperatures and pressures were investigated using a dynamic method, in which sc-CO_2 was continuously flowing through the extraction system. The sc-CO_2 extraction behavior and recovery of bio-oil and phenol were reported and discussed. The apparent solubility data of phenol in sc-CO_2 obtained in this study were also fitted to Chrastil, Adachi & Lu and Bartle equations. The correlation of solubility data using those equations were compared and discussed.

2. Materials and methods

2.1. Materials and chemicals

Bio-oil used in this study was supplied by Malaysian Palm Oil Board (MPOB), Bangi, Selangor, Malaysia and used in the experiment as received. It was derived from pyrolysis of PKS at 400 °C for residence time of 30 min using the Biochar Experimenters Kit (BEK), a multi-mode manual pyrolysis unit supplied by All Power Labs (USA). PKS is one of the major solid biomass wastes as a result of large-scale oil palm (*Elaeis guianensis*) plantations in Malaysia, which can be utilized for generation of biofuels and biochemicals [23]. Details of the equipment and pyrolysis process of PKS have been reported in our previous work [24]. Methanol (CAS 67-56-1) was of analytical grade (EMSURE® ACS, ISO, Reag. Ph Eur) and obtained from Merck, Germany. Pure liquefied phenol (CAS 108-95-2) obtained from R&M Chemicals was used as external standard for calibration and quantification. The chemical composition of the initial bio-oil (based on % peak area from GC-MS analysis) was reported in our previous work; 82.35% of phenolic compounds, 11.31% of acids, 2.97% of ketones, 2.14% esters, 0.44% of aromatic compounds, 0.79% of other minor compounds and water mass fraction of 20.97% [25].

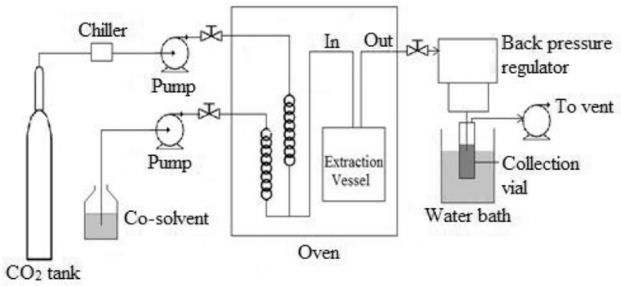

Fig. 1. Schematic diagram of experimental set-up for supercritical CO_2 extraction of bio-oil.

2.2. Experimental procedures

Extraction of bio-oil using sc-CO_2 was performed in an extraction vessel of 50 mL (Jasco, EV-3-50-2) at 50–70 °C and 30–40 MPa. The temperature and pressure range employed were slightly higher than the range studied in our previous reported work [25] as phenol (target compound in this study) has a high melting point of 40.9 °C and crossover pressure of 28 MPa [26]. In each experiment, raw bio-oil was mixed with clean 2 mm glass beads in the extraction vessel, which was placed in an oven (Memmert, Model: UN55 BO with precision of ± 0.1 °C) set at the desired extraction temperature. The chiller was set at 0–5 °C. Pure CO_2 (99%) was supplied to the extraction system by pump (Jasco, PU-2088-CO_2 Plus with relative standard deviation for flow rate precision within 2.0%). The pressure of the system was maintained by an automatic back pressure regulator (Jasco, BP-2080-Plus with pressure control precision of ± 0.2 MPa). The extraction time of 1 h was set based on our previous optimization study [25] and CO_2 flowrate of 4 mL min^{-11} was selected as it was considered low enough for the system to reach equilibrium for solubility measurements [27]. Fig. 1 shows the experimental set-up of the bio-oil extraction. Details of the equipment and experimental procedures are similar to our previous reported work [25]. After the extraction process, the system was depressurized slowly to ambient condition and the amount of bio-oil collected was weighed. All experiments were repeated twice to ensure reproducibility of the findings.

2.3. GC-FID analysis

Initial bio-oil and bio-oil extracts obtained at various conditions were quantitatively analyzed for their phenol contents using a 7820 A gas chromatograph (GC) system from Agilent coupled with flame ionization detector (FID) with relative standard deviations for peak area and retention time repeatability within 2% and 0.06%, respectively. Calibration was performed using pure liquefied phenol as external standard. Around 10 mg of sample was dissolved in 1 mL methanol and then injected into the column. The injector condition was set at temperature of 260 °C, split ratio of 50:1, and injection volume of 1 µL. Separation was carried out on a HP-5 column (part number: 19091J-413) with dimension 30 m × 0.320 mm × 0.25 µm. The oven temperature was set at 40 °C and ramped up to 300 °C at a rate of 5 °C min^{-11} and held for 5 min. Helium was used as carrier gas with constant flow of 1 mL min^{-11}.

2.4. Data analysis and model fitting

The experimental solubility of phenol present in the bio-oil extracts obtained at various temperatures and pressures was correlated using model proposed by Chrastil [28], Adachi & Lu [29] and Bartle [30]. Chrastil model is the first class of density-based model that predicts a linear relationship between the logarithm of solubility and the logarithm of solvent density which is used as a kind of standard model for solubility data representation [31]. It has been frequently used to