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Study on the physical and chemical composition of agro wastes for the production of 5-hydroxymethylfurfural

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ABSTRACT

Treated sludge, goat manure, sugarcane bagasse, empty fruit bunches of oil palm (EFBP) and dry leaves are agro wastes that have high potential for use as feedstocks for the production of 5-hydroxymethylfurfural (5-HMF). The focus of this study is to investigate the production of 5-HMF from agro wastes via co-hydrothermal (CHT) treatment and extraction. Present study include examine on agro waste's physical and chemical properties and also their thermal degradation behaviour. The analysis of the bio-oil products is conducted by FTIR and GC–MS. Co-hydrothermal experiments were conducted at a temperature of 300 °C with an experimental time of 15 min, followed by alcohol extraction. Highest carbon and hydrogen content are 45.94% and 6.49% (dry leaves) with maximum high heating value 18.39 MJ/kg (dry leaves) and fix carbon value 6.60 (goat manure). Through CHT about 39% 5-HMF, 22.97% carboxylic acids, 0.97% of aromatic and 0.73% aldehyde obtained.

1. Introduction

As the fourth largest primary energy source, agro waste has great potential to replace fossil fuels and become feedstocks for the production of bio-fuels (Shamsul et al., 2014). Sewage sludge, animal manure, sugarcane bagasse, empty fruit bunches of oil palm and dry leaves cause environmental pollution due to increasing human population, intensification of livestock practices and high demand for agricultural products (Yin et al., 2010). In addition to environmental issues, the finite stock of fossil fuels worldwide has become a critical issue, and thus a renewable resource is needed as a feedstock for bio-fuel (Bhaskar et al., 2011). Moreover, the fluctuation in the price of fossil fuels and the high demand for this fuel (34.90 billion barrels of fuel expected to be used in 2030) led to a decrease in fossil fuel reserves (Zhao et al., 2014a,b). Therefore, it is suggested that agro wastes be converted into 5-hydroxymethylfurfural (5-HMF) via co-hydrothermal (CHT) treatment; potential technology for the conversion of agro wastes to 5-HMF without prior drying (Zhao et al., 2014a,b) operate at low temperatures compared to pyrolysis and gasification methods (Zhao et al., 2014a,b). During CHT treatment, biochemical compounds (e.g., lipids, proteins and carbohydrates) present in agro wastes undergo hydrolysis, repolymerization, dehydration, decarboxylation, and deamination to form energy-dense crude bio-oil that is rich in organic carbon (Selvaratnam et al., 2015).

The 5-hydroxymethylfurfural (5-HMF) is a valuable biomass-derived compound that forms via the dehydration of carbohydrates (glucose, fructose, cellulose and sucrose) (Okano et al., 2013). This 5-HMF intermediate compound is usually used in the production of plastic, pharmaceuticals, fine chemicals and liquid fuels (Liu et al., 2012). 2,5-Dimethylfuran derived from 5-HMF contains an energy of 31.5 MJ L^{-1}, which is higher than that of ethanol (23 MJ L^{-1}) and close to that of gasoline (35 MJ L^{-1}) (Tan, 2016). The production of 5-HMF from fructose and glucose has already been discussed in previous studies (Okano et al., 2013; Liu et al., 2012), but there are some challenges in the current production method. Recent reports have illustrated that the main obstacles faced when using catalysts are as follows: (1) side reactions form levulinic acid (LA) and humin when using aqueous solution [HCI, H_2SO_4, H_3PO_4] (Tan, 2016; Greetham et al., 2016); (2) the separation process is toxic, expensive and consumes a large amount of energy and the products are insoluble when using organic solvent [DMSO, DMF] or ionic liquids ([EMIM]CI) (Tan, 2016; Cao et al., 2013; Qu et al., 2012); (3) regeneration and disposal is difficult when using a homogeneous acid as the catalyst [Lewis acids, mineral acids, organic acid salts] (Zhu et al., 2011); and (4) the activity and selectivity of heterogeneous acids are unsatisfactory in water [ion-exchange resins, zeolites, metal phosphate and metal oxides] (Yang et al., 2011). Note that efficient catalysts for the production of HMF from fructose are rarely active for glucose, and low HMF yields are

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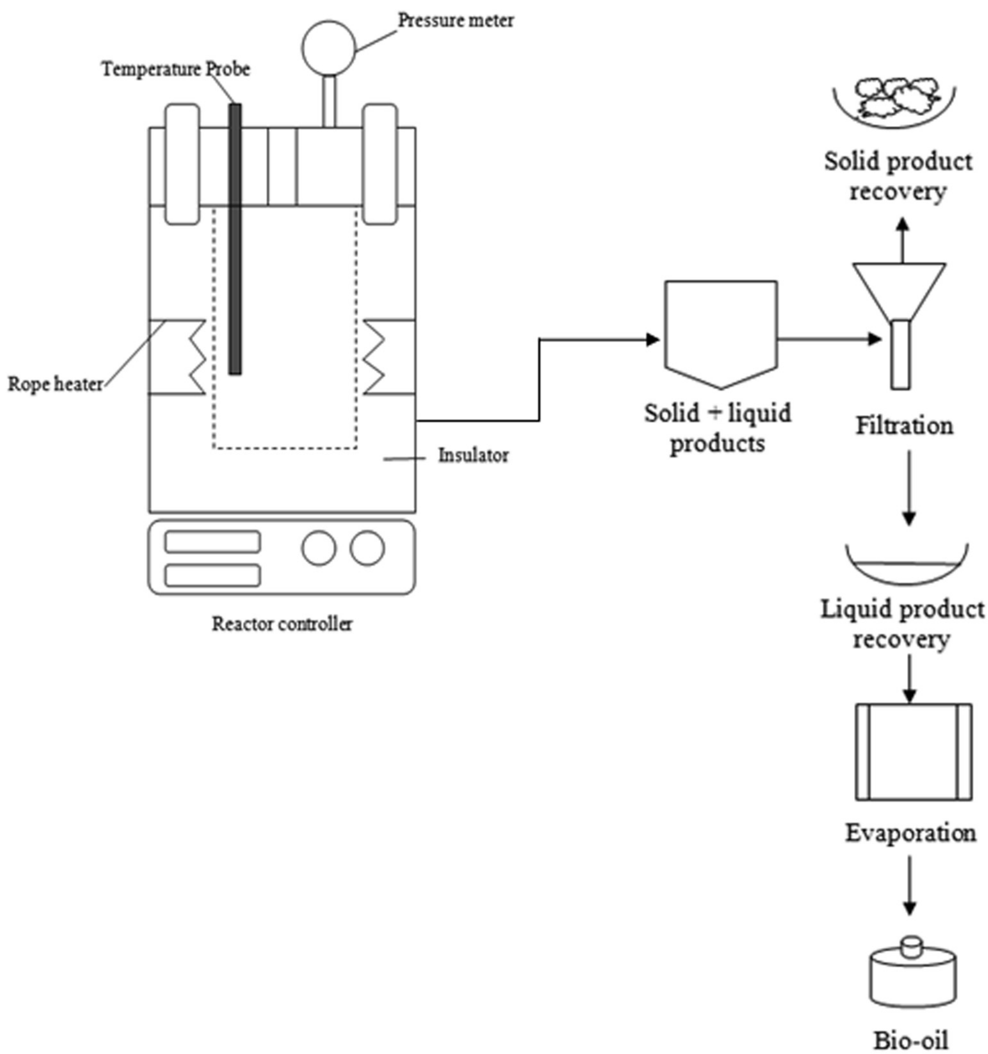

Fig. 1. Schematic diagram of co-hydrothermal (CHT) and extraction.

obtained (Fernanda et al., 2014). Therefore, the homogeneous base NaOH is suggested as the catalyst to reduce the formation of by products, reduce the cost and make the system easier to handle (Ibrahim et al., 2015).

Most previous studies used monosaccharides (fructose and glucose) as the feedstock, but a lignocellulosic biomass feedstock to form 5-HMF was suggested by a previous study. Toker et al. (2013) studied grape, mulberry, black mulberry and carob molasses as feedstocks for the production of 5-HMF using water without any heat or acid. Rasmussen et al. (2016) performed the hydrothermal pretreatment of empty fruit bunches of oil palm to obtained less than 10 wt% 5-HMF. In another case, Antonetti et al. (2015) obtained 12 wt% 5-HMF by the hydrothermal treatment of giant reed and 3.09 wt% 5-HMF by using sugarcane bagasse as the raw material (Iryania et al., 2013). However, no study has been conducted on the co-hydrothermal treatment of agro wastes mixed together in a single reactor to form 5-HMF.

Therefore, the present study purposes an environmentally friendly process for the conversion of agro wastes into 5-HMF by direct co-hydrothermal treatment and extraction. To replace the use of glucose, fructose or hexose as the feedstock, experiments were conducted using single and mixed agro wastes, such as sugarcane bagasse, dry leaves, goat manure, sludge and EFBP, as the raw material. The characterization of agro wastes is conducted in terms of their physical and chemical properties, higher heating values and thermal degradation analysis. In this study, the co-hydrothermal (CHT) treatment of agro wastes is conducted with NaOH solution, followed by extraction using methanol solvent; methanol, a low boiling point solvent, is easy to separate and recycle. The qualitative analysis of bio-oil produced by single-feedstock hydrothermal treatment is compared with that produced by co-hydrothermal treatment using Fourier transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Physical and chemical analysis

All solid wastes were obtained from the following suppliers: treated solid sludge samples were from the Indah Water Consortium; goat manure samples were from Dengkil farm; sugarcane bagasse was from Jenderam village; empty fruit bunches of oil palm were from the production of palm oil by Malaysia Palm Oil Berhad; and dry leaves were from the Alam Flora Company. All samples were mechanically pretreated to remove impurities, such as sand, small rocks and hard wood. The sizes of the samples were between 2 and 3 cm without extra water. For the chemical composition analysis, the elemental compositions of carbon, hydrogen, nitrogen, sulphur and oxygen were determined by a CHNS analyser (LECO model CHNS-932) from the Faculty of Science Technology, National University of Malaysia. Chemical composition analysis is necessary to confirm the degree of conversion by comparing the elemental values of carbon, hydrogen and nitrogen. Additionally, physical analysis of the samples, consisting of analysis of the moisture, total solid, volatile, ash and fixed carbon content, was conducted