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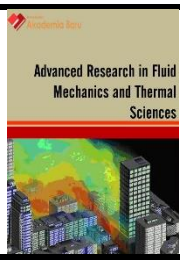

Simultaneous Hydrolysis Reaction and Thermal Characteristic of Fibre Solid Residue in Hot Compressed Water Extraction

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ABSTRACT

Crude palm oil (CPO) was extracted from palm mesocarp by use of hot compressed water (HCW). The extraction time was set to 60 mins, the temperature from 393 to 435 K, and the pressure 3, 4, and 5 MPa. The maximum CPO yields 0.5410 ± 0.0046 g-oil/ g-dried mesocarp with free fatty acid (FFA) of 0.8072 ± 0.0764 %. Simultaneous hydrolysis reaction of mesocarp fiber was occured during the extraction process, and glucose and alcohol were also obtained. Thermal characteristic of solid residue was observed at the different temperature through its structural group analysis. The result suggested that a zero waste processes can be developed by use of HCW.

1. Introduction

Over half century, palm oil industry has significantly contributed to the Malaysian economy with the production of 20 million tonnes crude palm oil (CPO) at the trade value of RM 47 billion in 2014. In Malaysia, mechanical screw press system is utilized as a CPO extraction method after several pre-treatment process such as sterilization and it contribute an overall oil losses estimated up to 7% or 0.07 (g-oil /g-dried mesocarp) [1]. Thus, various researchers are introducing others extraction options such as supercritical CO2 and others. However, the current potential solutions seem to be ended up in the research scale due to several reasons mainly related to economical constraint and process sustainability. Thus, it is essential to establish an alternative process for possible improvement on CPO extraction. In this study, the effect of temperature and pressure in the hot compressed water extraction (HCWE) to CPO yield was evaluated. In order to understand the process, the analysis are

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also conducted for water based sample after the process to analyzed sugar and alcohol concentration. The residue fibre from the extraction was analysed at a the different HCWE temperature to show the relation of the fibre functional group as the temperature increased.

2. Methodology

2.1 Material and Method

Oil palm fresh fruit bunch (FFB) was collected from Felda Mempaga Satu, Bentong, Pahang, Malaysia. Figure 1 shows a schematic diagram of HCWE apparatus. The HCWE was conducted at the fabricated equipment in Shizen ikohza, UTM, Malaysia [2,3]. The procedure was written below.

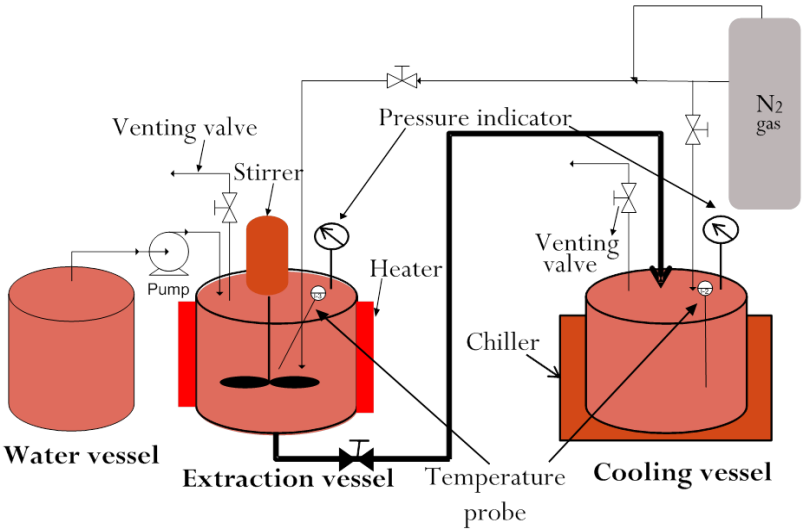

Fig. 1. HCWE facility

A 100 g of the shredded palm mesocarp was weighed, and loaded into the extraction vessel. After that, 500 cm^3 of distilled water was added into the vessel. The experimental temperature range was from 393 to 453 K, and the pressure was set to 3, 4 and 5 MPa. The extraction was conducted in semi-continuous process for 60 mins with 10 mins interval. Then, the sample was agitated with the impellor speed of 500 rpm. The extract was subjected to the post treatment after the extraction to obtain the CPO [2]. The CPO yield was calculated by Eq. (1).

$$\text{CPO yield} = \frac{V_{oil} \times \rho_{oil}}{W_s} \quad (1)$$

where V_{oil} is volume of CPO collected from HCWE process, ρ_{oil} is density of CPO and W_s is weight of palm oil mesocarp. The free fatty acid FFA analysis was done by MPOB standard titration method [5]. The procedure assumes FFA to compose solely of palmitic acid using Eq. (2).

$$\text{FFA} = \frac{25.6 \times V_{NaOH} \times M_{NaOH}}{W_{oil}} \quad (2)$$

where FFA is the free fatty acid percentage (FFA %), V_{NaOH} is the volume of sodium hydroxide (cm^3) used at the titration, M_{NaOH} is the molarity of sodium hydroxide (M) and W_{oil} is the weight of the oil (g).

Analysis sugar, namely glucose, in water sample was conducted using HPLC 1100 series (Waters, USA) with Refractive Index (RI) detector (Waters, USA) adapted from Muda (2015). A Shodex Sugar

SP0810 column (NREL, Japan) and mobile phase of deionised water with flowrate of 0.8 ml/min was used [4]. 2 ml of the water layer was filtered using syringe filter (Nylon, 0.45 µm). 10 µL of filtered solution was injected into the HPLC. Prior to that, the calibration curve was developed using glucose standard (Friedmann Schmidt, UK) to quantify the concentration of the sugar in the sample.

The concentration of alcohol components namely methanol, ethanol and propanol in water was analyzed using GC 7890 B system (Agilent technologies, USA) with the FID detector (Agilent technologies, USA) and headspace sampler 7697 A system (Agilent technologies, USA) adapted from Muda [4]. The DB-SELECT 624UI column (Agilent technologies, USA) at the temperature of 533 K and helium as the carrier gas was used. Meanwhile, the purified air and hydrogen was used in the FID ignition. 1 ml of sample and standard each time was transferred into headspace vial and crimped, and placed into the headspace sampler with the setting temperature of 353 K. The quantification of the compounds was integrated from the calibration curve.

The analysis of the functional group in the solid residue was analyzed using FTIR spectrometer (Perkim Elmer Spectrum 100 Series, USA). Before the sample analysis, an empty sample holder was scanned for the blank reading. The solid sample was scanned from 650 to 4000 cm^{-1} at 4 cm^{-1} resolution in the room temperature.

3. Results

3.1 Effect of HCWE Temperature and Pressure on CPO Yield and Analysis of Water

The HCWE process produced Figure 2 is shown the effect temperature on the CPO yield at constant pressure of 3, 4 and 5 MPa. It can be observed that CPO yield using HCW was between 0.4100 to 0.5410 (g-oil / g-dried mesocarp) for the temperature and pressure range studied. The CPO yield increases significantly by 17.21 % from the temperatures of 393 to 433 K from 0.4545 ± 0.0065 to 0.5327 ± 0.0065 (g-oil / g-dried mesocarp) respectively at the pressure of 3 MPa. Above 433 K, the CPO yield decreases gradually to 0.4833 ± 0.0065 (g-oil / g-dried mesocarp) at the temperature of 453 K at the same pressure. It was observed that HCWE at 50 MPa gives the maximum yield of 0.5410 ± 0.0046 (g-oil/ g-dried mesocarp) at 433 K. Generally, the temperature had shown the significant effect to the CPO yield. However, the pressure in the studied range of 4 to 5 MPa is not given the significant effect. The analysis of FFA for sample at the 433 K and 50 MPa condition had obtained the value of 0.8072 ± 0.0764 %. However, the CPO yield are still low due to the loses of the oil in solid and oil-water emulsion [2].

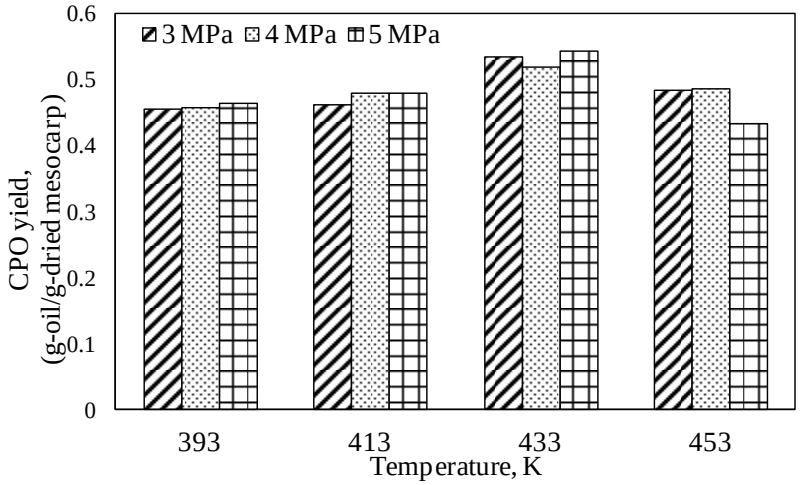

Fig. 2. The effect of temperature to the CPO yield at constant pressure of 3, 4 and 5 MPa

Figure 3 shows the result of glucose analysis for the water sample. The concentration of glucose is increased from 1.08 to 2.83±0.06 mg-glucose/g-dried mesocarp as the temperature increased from 393 to 453 K.

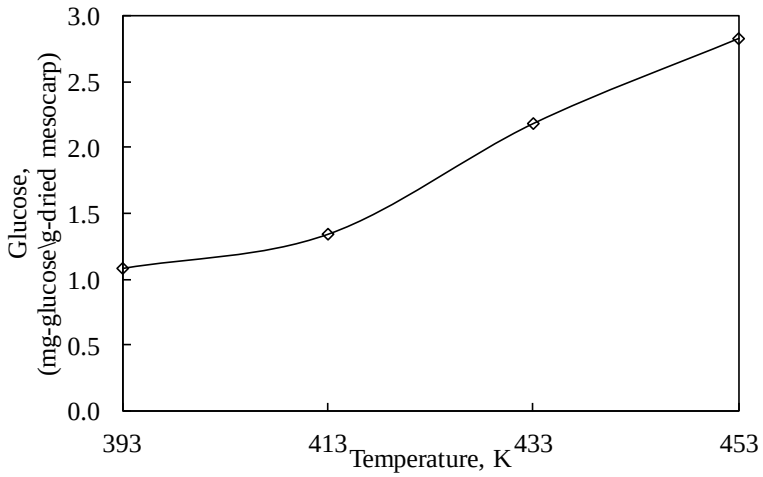

Fig. 3. The effect of temperature to the glucose concentration in water sample at 5 MPa

Figure 4 shows a reaction scheme during HCWE. The increasing of the glucose is possibly caused by the cellulosic hydrolysis reaction of mescocarp fibre to glucose. In fact, the mesocarp fibre is generally consist of 42.8 % of cellulose, 33.1 % of hemicullose and 20.49 % of lignin [6]. Therefore, this would create the sustainability of the industry. Apart being used as a sugar source in the food industry with the designated purification process, this compound is also a valuable source in the bioalcohol production using fermentation process. Bioalcohol is known as biofuel which became the alternative fuel for the fossil fuel. Currently, this fuel was produce using the first generation biofuels such as corn, sorghurm, sugarcane and barley which mainly are food source. This situation invited various controversial issues regarding world food supply which converted to the fuel. Thus, HCWE is potential to became the zero-waste process by providing the useful liquid waste. Not limited to that, some alcohol was detected in the analysis of the water.

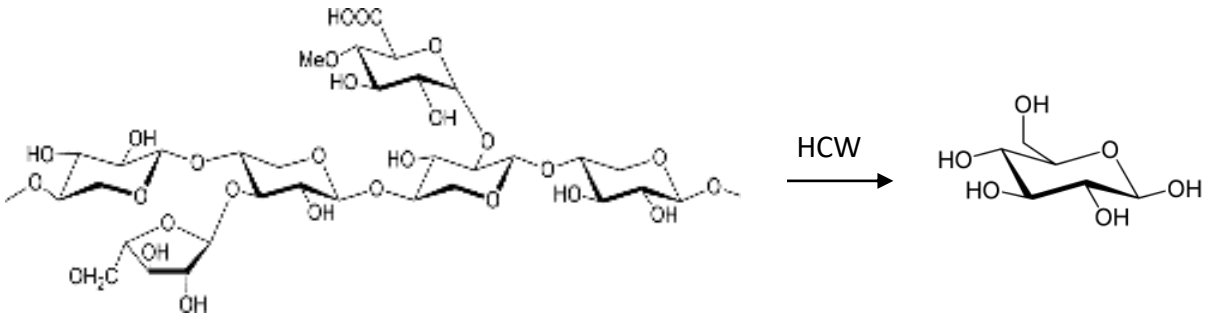

Fig. 4. Hemicullose hydrolysis during HCWE process

3.2 Alcohol Concentration in Water Sample

As shown in the Figure 5, a higher concentration of methanol is detected followed by ethanol and only less than 0.03 kg/m^3 of propanol is detected in the temperature of 433 and 453 K, and constant pressure of 5 MPa. As the temperature increase from 433 to 453 K, the concentration of methanol

was increased from 1.64 to 2.30±0.06 kg/m3. However, the temperature has no significant effect to the concentration of ethanol at an average concentration of 0.37±0.01 kg/m3. The result showed the same tendency as that of Phaiboonsilpa *et al.,* where the higher concentration of alcohol promotes the hdyrolysis of nypa frond using HCW [7]. The existence of the alcohol component in the water sample, especially methanol, had strengthen the possibilities of the bioethanol production using this wastes. Futhermore, the simulatenous production of biodiesel from palm mesocarp can be furthered investigated for possible transesterification of CPO with an addition of catalyst such as potassium hydroxide [8]. Hydrolysis also contributed to the mesocarp cell wall fracture which enchance the entrainment of the CPO during the extraction process [2]. The result well described the extraction mechanism during the CPO extraction using HCW.

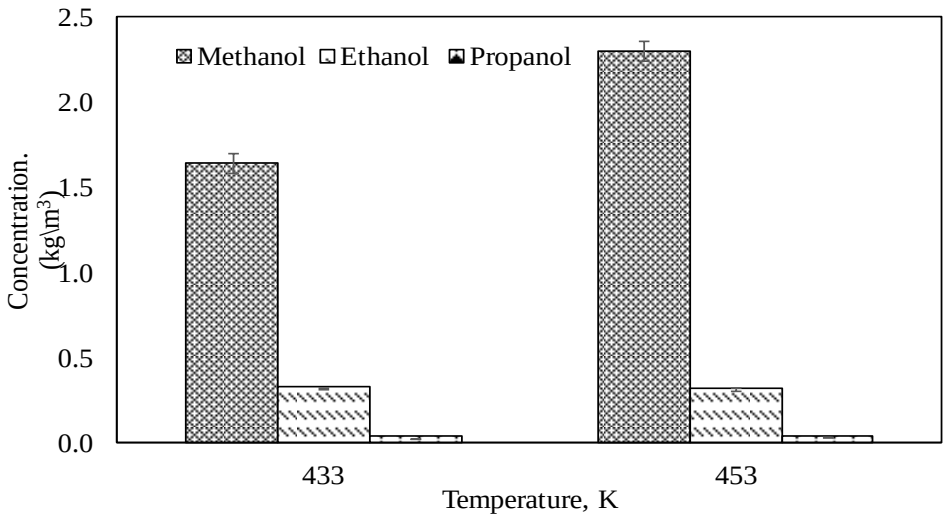

Fig. 5. The effect of temperature to the alcohol concentration in water sample at constant pressure of 5 MPa

3.3 Thermal Characteristic of Solid Residue Fibre

Absorbance band for solid residue fibre functional group at the different temperature is shown in Figure 6. At all the temperature tested, the appearance of the hydrogen vibration of C-H group which attributed to aliphatic methylene group in the solid residue at absorption band of 2916 and 2851 cm^{-1} in FTIR spectra for all sample from 120 to 180◦C as shown in Figure 6. This group is believed to be fat and lipids component [9,10]. Therefore, the increasing of solid residue would reflect to higher fat and lipids component. Meanwhile, the absorption band at 1742 cm^{-1} was believed to be indicated for metabolics products such as aldehydes, ketones, and ester which come from the degradation of hemicullulose fibre cause it was initially available in the palm oil fibre such as EFB [10,11,12]. Not limited to that, the increasing of IR spectrum at the band of 1374 cm^{-1} as the temperature increased is a vibration of N-O stretching [13]. This nitrate component is believed to be accumulated during the decomposition of fibre as observed in EFB decomposition process [13]. The peak band of 1460 and 1420 cm^{-1} is believed to be a lignin characteristic as observed in wood chips [9]. It also reported that band of 1420 cm−1 is attributed to the amorphous cellulose II and crystallized cellulose I which believe resulted from the degradation of fibre [9,14]. Besides that, in the band of 1115 cm which atributed to the aromatic in-plane deformation or σC−H is also believed to be part of lignin structure [10,15].

Therefore, the increasing of these absorption band as temperature increased is due to the increasing of the fibre cell fracture. The band of 892 cm^{-1} was attributed to a β-glycosidic linkage between the

sugar units and believed comes from the hydrolysis of hemicellulose [10,16]. Meanwhile, the band of 1635 cm^{-1} is attributed to the adsorbed water [10,16].

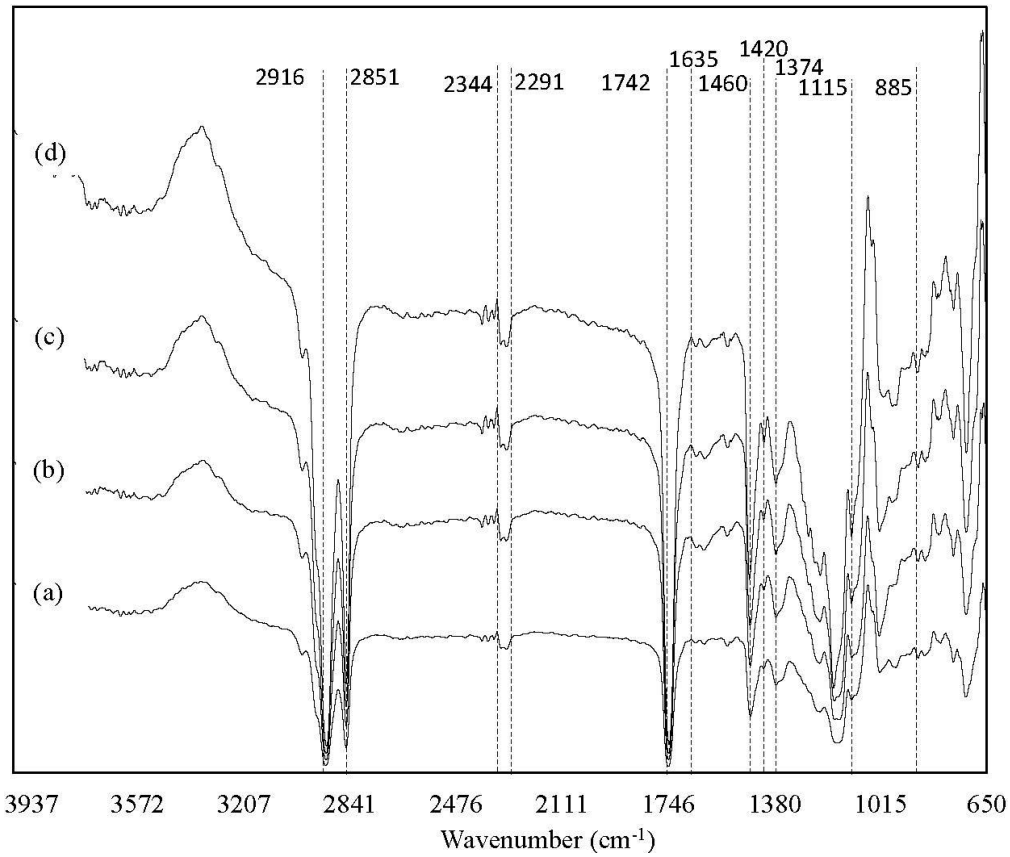

Fig. 6. FTIR spectra of solid residue sample at constants pressure of 50 bar and different temperature (a) 120◦C (b) 140◦C (c) 160◦C (d) 180◦C

4. Conclusions

The HCWE is a potential process in special grade CPO but further work is required to improve on the oil recovery through reduction in oil losses in the emulsion and in the water. HCWE can creates the sustainability in palm oil industry by produce the CPO as a main product and generate the biofuel from it wastes. The thermal characteristic of the solid residue fibre show the possible thermal hydrolysis for this cellulosic material to sugar and alcohol.

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