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Production of phenolic compounds from durian peel waste using sub-critical water

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Abstract

Due to the little or no commercial value, durian residues are disposed in open spaces and/or in municipal waste stream causing environmental pollution in Malaysia. Durian peel waste (DPW) which accounts for about 65-70% of the whole fruits contained value addition substances such as phenolic compounds (PC). To determine the optimum temperature and time for recovery of PC from DPW, Sub-critical water (SCW) extraction was carried out under reaction temperature (100-360°C at 4 min fixed time) and time (1-30 min and 240°C fixed temperature). After reaction, two main phases were isolated, residual solid and water soluble phases. The aqueous phase was analyzed for PC and total organic carbon (TOC) contents. The results revealed that the maximum PC yield using SCW was 34.600 mg GAE (Gallic acid equivalent)/g at 240°C, 25 min. Moreover, from the results of TOC it shows that with increasing temperature, the TOC yield increase, this indicated that the process proved to be a good technique for conversion of biological waste into value addition materials such as phenolic compounds.

Keywords: durian peel, phenolic compounds, sub-critical water treatment, hydrolysis reaction, pyrolysis reaction

INTRODUCTION

Durian (*Durio Zibethinus Murray*) is believed to be a native fruit of South East Asia and one of the most popular fruits which are grown and consumed in raw or processed into different types of edible products. Durian, fruit of several tree species, is belonging to the genus Durio in a family of Bombacaceae. People revered it as the "king of fruit" because of its large size, unique odor, and formidable thorn (Foo and Hameed, 2012).

Malaysia is producing large quantity of durian fruit per year for several purposes. Recently, Manshor et al. (2014) reported that, Malaysia produced approximately 320,164 MT of durian in 2013. This produces massive residue in the form of durian peel, seeds and rink. These durian waste constitutes 65-70% of the entire fruit with an average total weight of about 255,353 MT all over the country, hence increasing landfill loading rate (Foo and Hameed, 2011; Foo and Hameed, 2012). Due to the less or no commercial value, durian residues are disposed in open spaces and/or in municipal waste stream causing environmental pollution. With more stringent and restrictive environmental regulations concerning the pollution from agricultural waste materials by regulatory agencies (Foo and Hameed, 2011), from ecological and economic point of view, it is beneficial to convert these residual wastes into useful materials.

Alvarez and Saldaña (2013) reported that agricultural waste including durian peel to be very rich source of phenolic compounds, carbohydrates and different types of antioxidant compounds. An efficient, inexpensive, and environmentally friendly way to use these fruit residues is by converting them into soluble sugars, phenolic compounds and other value added material. These products could be utilized as a substrate for fermentation process,

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bioethanol productions and served as raw material for pharmaceutical, food industry to enhance the sensory and nutritional values of foods and cosmetic industries (Laopaiboon et al., 2010).

The traditional methods for extractions of bioactive compounds includes; maceration, hydro distillation and soxhlet extraction (Ruiz et al., 2014). Extraction solvent mainly are acetone, methanol, ethanol, ethyl ether, acetate and many more (Pourali et al., 2010). Generally, the uses of the methods mentioned earlier were reported to be expensive, time consuming, inefficient, and some time it has some negative aspects. The drawback of those methods has led researchers to investigate alternative technology that could be utilized favorably in terms of cost, efficient, ease of operations and environmentally friendly techniques (Don et al., 2014) .

Therefore, in an effort researchers developed and explored new powerful technique called Sub-Critical Water (SCW) treatment technology. SCW is defined as hot water at heating temperature between 100 to 370^{0}C and under enough high pressure 22.1 MPa to maintain water in the liquid state (Ravber et al., 2015). SCW in this state was reported to possess unique properties, such as its dielectric constant decreases to the same as ethanol, which make it acts as a solvent and it magnitude of ion product is high (He et al., 2012). Recently, many valuable materials have been produced from various agricultural waste materials using SCW treatment technology such as production of soluble sugars from rice bran (Pourali et al., 2010), reducing sugar from bagasse waste (Zhu et al., 2012) and biodiesel production (Woo et al., 2014). Therefore, SCW might be a reasonable alternative and promising method for efficient decomposition of durian peel for phenolic compounds production.

To the best of the author's knowledge, from the literatures reviewed there is no any report about productions of phenolic compounds from durian peel using SCW treatment technology. Therefore, in the present work we decomposed durian peel waste and recovered phenolic compounds under SCW conditions. Total organic compound (TOC) of the aqueous solutions was also investigated.

MATERIALS AND METHODS

Chemicals

99.9% Methanol, Sodium bicarbonate (Sodium hydrogen carbonate), 95% ethanol, hexane, and 98.8% acetone were all purchased from Fisher Scientific (M) Sdn. Bhd. (Malaysia). Gallic acid as phenolic compound standard and Folin - Ciocalteu's phenol reagent were purchased from Scienfield Expertise PLT, Selangor. (Malaysia).

Sample preparations

Fresh durian fruits were collected from Taman agriculture University Putra Malaysia (UPM). The durian peel waste was washed and cut into small size with knife and then was grounded with a dry mill (Panasonic MX-SM1031) into smallest suitable size to ease charge into the reactor average 5-10 mm and homogeneous.

Sub- CW treatment

Sub-CW treatment was carried out in a standard stainless steel batch reactor (SUS316, id. 16.5 mm×150.4 mm) ready made from Swagelok & Co. 3.3 g of sample and 21.54 ml of distilled water were placed in to the reactor, then air was forced out of the reactor by purging argon gas. The reactor was capped and tighten properly, then dipped into a heated oil bath (Thomas Kagaku Co. Ltd.) for reaction temperatures of 100 to 180°C and in preheated salt bath (Thomas Kagaku Co. Ltd.) of 200-360°C for 4 min reaction time, then at 180 and 240°C for 1-30 min. After the preferred reaction time was reached, the reactor was then taken out from the heating bath and immediately cooled down by immersing in a cold water at ambient temperature (Pourali et al., 2009). Steam table was used to determine the treatment pressure.

Reactor content isolation after Sub-CW treatment

After SCW treatment, reactor contents were transferred into a glass test tube in a carefully manner to avoid any loss of the aqueous and remained solid. The products were isolated into two phase water soluble and residual solids. The separation procedure was briefly performed as follows; the glass test tube was centrifuged at 1500×g for 10 min, and then the supernatant and residual solid were separated by transferring of the aqueous solution to another test tube using Pasteur pipette. The aqueous phase was also centrifuged at 2000×g for 5 min for the second time and then filtered with a 0.2-μm filter paper, and then the aqueous product was kept in a freezer for further analysis. Finally, the residual solids were kept in a heating oven at 60°C for two days to dry up the remaining liquid and the final weight was measured and recorded. The solid residue was obtained using equation 1 shown.

$$\text{Solid residue} = \frac{\text{weight of solid phase (g)}}{\text{Weight of sample (g)}} \qquad (1)$$

Analysis

1. Total phenolic contents determination

The total phenolic contents of the aqueous product was determined using the Folin-Ciocalteu phenol reagent methods reported by (Budrat and Shotipruk, 2009). Briefly described as follows, 0.1 mL of the aqueous solution was mixed with 0.1 mL of Folin-Ciocalteu (F-C) reagent and 2.8 mL of distilled water. The mixture was allowed to stand for 5 min. Then 2 mL of aqueous sodium hydrogen carbonate (Na_2Co_3 3g /100 mL) was added into the mixture. The mixture was then shaken using tube shaker and incubated for 90 min in the dark at room temperature where by wrapping it with aluminum foil to allow complete reaction. Then the mixture absorbance was determined using UV-Vis recording spectrophotometer (UV-160A Shimadzu, Japan) at 750 nm. The concentration of the obtained produced was reported as GAE mg/g dry sample.

2. Total Organic Carbon (TOC) and pH Measurements

The pH of the supernatant phase after separation was determined using a Horiba pH meter F-52 (Horiba Co., Japan). The TOC level in the supernatant phase was determined using an automatic total organic carbon analyzer (Shimadzu, TOC-V CPH. Shimadzu co., Japan). The TOC yields in mg/g dry sample were calculated following equation 2.

$$TOC\ yield = (\text{TOC} \ast \text{V})/\text{W} \qquad (2)$$

Where: TOC, V, and W denoted the TOC of the aqueous phase in mg/L, Volume of the aqueous phase in L and Weight of dry sample in g respectively.

RESULTS AND DISCUSSION

Effect of temperature and time

1. Phenolic contents yield

To determine the influence of SCW temperature on the production of phenolic compounds from durian peel waste, sequences of experiments were carried out in the range of 100-360°C at a fixed reaction time of 4 min. Figure 1 shows the cumulative yield of the total phenolic contents produced. At the beginning the amount obtained was slightly small. However, with further increased in treatment temperature from 160 to 240°C there was a significant increase in the yield from 2.60 to higher amount of about 33.70mg GAE/g. As reported by Yoshida et al. (2014) the noticeable increase of the phenolic contents could be associated with the decreased in the polarity of SCW at higher temperature, that resulted the higher solubility of the phenolic compounds in the water.

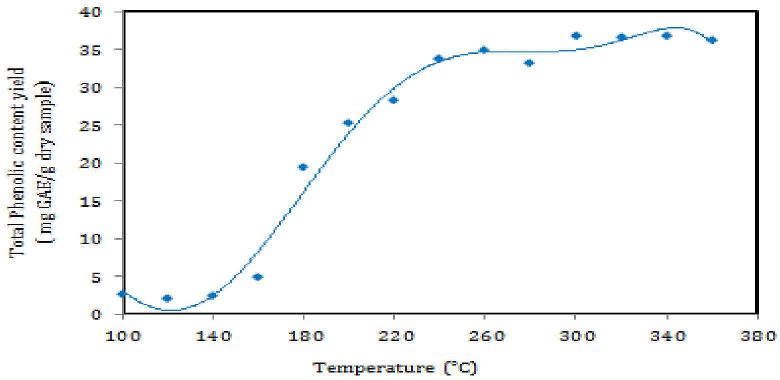

Figure 1. Effect of SCW temperature on the total phenolic compounds production at 4 min reaction time

However, it also appears that from (Figure 1.) when reaction temperatures increased beyond 240°C there was no significant enhancement of the phenolic contents. The evidence suggests that decomposition of the entire available produced total phenolic compounds from the peel might result in the unchanged yield within this temperature range. This is consistent with results obtained in previous study (Pourali et al., 2010). Budrat and Shotipruk (2009) also observed degradation of product at treatment temperature between 200-230°. They recovered phenolic compounds using SCW from bitter melon at temperature from 130-230°C. Higher recovery of phenolic contents of 54.90 mg/g was recorded at 200°C production temperature. But they reported that with further increase of temperature to 230°C the recovery of phenolic contents drops to 32.63mg/g.

The time course of the production of total phenolic compounds was also investigated by varying the time from 1-30 min at a fixed reaction temperature of 240°C. (Figure 2) shows the result. The phenolic contents yield increased rapidly to 33.70 mg GAE/g at 4 min. After this time, production almost remained constant until 20 min. When it reached 25 min, there was slight improvement of the yield due to the decomposition of lignocellulose complex fraction. This observation is supported from previous studies reported by (Prado et al., 2014a; Prado et al., 2014b). Low yield of phenolic contents was found at 30 min. This might be due to increases loss of phenolic by oxidation (Al-farsi and Lee, 2008). Therefore, 240°C reaction temperature at 25 min is the best optimum conditions for the decomposition of durian peel for phenolic compounds production using SCW.

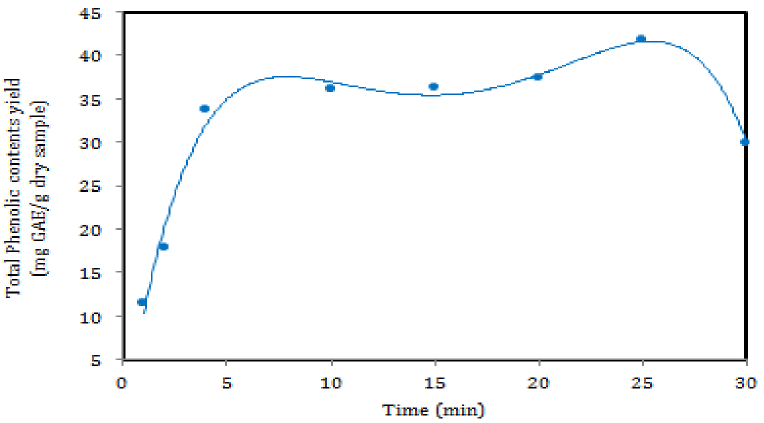

Figure 2. Time course for the total phenolic compounds production at 240°C reaction temperature

2. Total Organic Carbon (TOC)

Figure 3. Presents the effect of SCW temperatures on TOC yield at 4 min constant reaction time. After phase isolation, soluble organic materials present in the water phase were

measured using TOC analysis. At the beginning the TOC yields slightly increased from 1.87 to 3.30 mg/g when temperature increased from 100 to 180°C, then increased steadily to 3.67 mg/g with further increase of reaction temperatures to 260°C. Moreover, rapid increase of TOC concentration can also be observed with increasing temperature above 260°C and reached peak yield of about 6.50 mg/g at 360°C. This is in good agreement with results obtained in previous studies (Pourali, 2010; Yoshida et al., 2014). This shows that most of the water soluble organic carbons are transferred to the liquid phase due to the decomposition of large macromolecules of the durian peel. It was found that with an increase in temperature the amount of solid residue decrease while TOC yield increase.

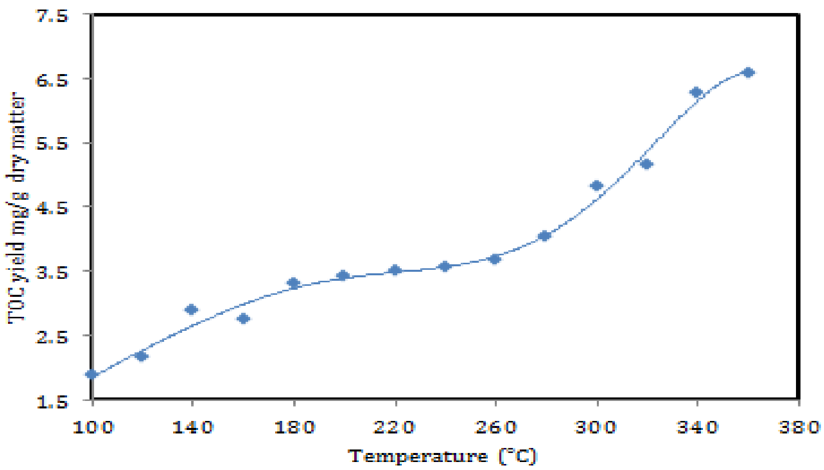

Figure 3. Effect of SCW temperature on TOC yield at 4 min reaction time

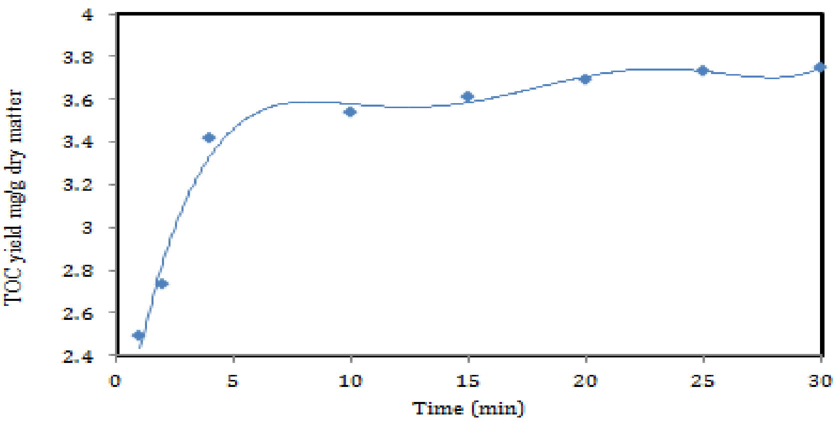

Figure 4. Time course of TOC yield at 240°C reaction temperature

TOC in the liquid phase was measured with different reaction times at 240°C temperature and the results are given in (Figure 4). TOC yield increased sharply to 3.541 mg/g with an increase in reaction time 4 min. The results suggested that carbon component of the peel decomposed to water soluble components gradually by SCW hydrolysis reaction (Tavakoli and Yoshida, 2008). However, with longer reaction time the amount of TOC yield almost remains the same. In a similar manner Sereewatthanawut et al. (2008) under SCW condition produced amino acids and protein from deoiled rice bran. They reported the increase in TOC yield at the retention times below 30 min.

CONCLUSIONS

The following conclusions can be drawn from the study:

- We found that SCW treatment technology was successfully utilized by the decomposition of durian peel waste for the production phenolic compounds under different reaction temperatures and times.

– The yield of total phenolic contents in the products increased significantly with increasing temperatures within a short reaction time of 4 min. this could be attributed to decrease in dielectric and ionization constants of water which increased the solubility of hemicellulose part of the peel waste into the aqueous phase.
– Moreover, from the results of total organic carbon (TOC) it shows that with increasing temperature, the TOC yield increase, this indicated that the process proved to be a good technique for conversion of biological waste into value addition materials such as phenolic compounds. The phenolic compounds are good feedstock for pharmaceuticals & cosmetic industries.
– Consequently, our study shows that SCW is a promising techniques being a clean does not employs organic solvent, green alternative process for material recovery, environmentally friendly and less time consuming.

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