Fuel 163 (2016) 88–97

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Chemical, dielectric and structural characterization of optimized hydrochar produced from hydrothermal carbonization of palm shell

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HIGHLIGHTS

- Hydrochar production from hydrothermal carbonization of palm shell is optimized.
- Temperature is found to be most effective parameter.
- Dielectric properties are temperature dependent.
- The surface characteristics of the hydrochar was much improved.

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 6 July 2015
Accepted 20 August 2015
Available online 9 September 2015

Keywords:
Optimization
Palm shell
Agricultural waste
Hydrothermal carbonization
Hydrochar
Dielectric properties

ABSTRACT

This paper primarily investigates the possible optimum conditions for maximum yield production of hydrochar through hydrothermal carbonization of palm shell. The hydrochar and the palm shell have been characterized to understand the effect of hydrothermal carbonization on palm shell and the chemical, the dielectric, and the structural properties of optimized hydrochar were examined. The effect of the reaction temperature, reaction time and biomass to water ratio was analyzed and optimized using the central composite design of response surface methodology. The optimized conditions for hydrochar production have been found to be 180 °C, 30 min, and 1.60 wt.%, temperature, time and biomass to water ratio, respectively. The findings showed that the temperature has a greater influence over the efficiency of hydrochar production than time and biomass-to-water ratio. The porosity of raw palm shell increased remarkably through hydrothermal carbonization. The dielectric constant of palm shell and hydrochar was decreased with an increase in frequency.

1. Introduction

Hydrothermal conversion of biomass has gained the attention of researchers, owing to the advantages offered by both biomass and hydrothermal processes. The required form of the product and type of feed biomass are considered as a basis for the process selection [1]. Palm shell has been selected as the feed biomass for the current work. Ample quantities of biomass waste from the palm oil milling industry are produced in the form of empty fruit bunches (EFBs), palm shells, palm mesocarp fiber and palm oil mill effluent [2], which need to be utilized properly. The main product of choice is a solid product known as hydrochar thus, the process selected is hydrothermal carbonization. The hydrothermal carbonization process produces a higher yield of hydrochar with higher energy efficiency, higher level of carbon recovery, and lower ash content [3,4].

The dielectric properties of material determine the absorption, the energy transmission and the reflection of materials with the electric field of electromagnetic waves. The dielectric properties also quantify the ability of materials to dissipate electromagnetic energy in the form of heat [5]. The dielectric properties describe the heating characteristics of material and also define the interaction between the microwave heating and materials. The knowledge of dielectric properties may help in designing the microwave processing system and predicting the product yield of the microwave process [6,7]. Knowing the dielectric properties may lead to different applications of materials, such as sensors and electronic packaging [7]. The dielectric properties of hydrochar might be useful for microwave processing of hydrochar. These

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http://dx.doi.org/10.1016/j.fuel.2015.08.057
0016-2361/

properties include dielectric constant, dielectric loss factor, penetration depth and tangent loss (tan δ). The dielectric constant is an estimation of the dielectrics to store electrical energy whereas the dielectric loss factor measures the loss of electrical energy in the dielectrics. The penetration depth is defined as the depth in the material at which the power carried by a forward-travelling electromagnetic wave of the specified frequency falls to 1/e of the value just at the surface. The tangent loss measures the ability of a material to convert electromagnetic energy into heat energy at a specific frequency and temperature [8]. It is observed that the dielectric constant and dielectric loss factor, which are dependent on the frequency and the efficiency of the material to interact with microwaves, are controlled by their magnitude. Thus, forming an essential parameter to find the dielectric heating of materials [9]. The moisture content present in materials also has a strong effect on the dielectric properties of materials. The dielectric properties decrease in materials with higher moisture contents [10]. The temperature, density, chemical and physical composition are also important factors that have an effect on the dielectric properties [8,9]. The dielectric properties depend upon the composition and structure of materials as well as on the process conditions like temperature [11]. Furthermore, the dielectric properties of many materials depend on the moisture content, bulk density and the association of the permanent dipole moment with water and other constituent molecules [12]. Although the dielectric properties of different biomass materials like EFB, palm shell, oil palm fibers and wood and biochars from different materials have been reported in the literature [7,9,13,14], to the best of our knowledge, to date, the dielectric properties of hydrochar from any type of biomass have not been discussed. It has been suggested by previous studies that the dielectric properties highly depend upon the change in frequency; therefore, in this study, the dielectric properties of palm shell and hydrochar by varying frequency from 0.5 to 16 GHz have been investigated. The objective of this study is the optimization of hydrochar production using hydrothermal carbonization and to study the dielectric properties of hydrochar. Additionally, hydrochar and palm shell are analyzed using elemental and proximate composition, Fourier transform infra-red (FTIR), Burner–Emmett and Teller (BET), thermo-gravimetric (TGA) and field emission scanning electron microscopy (FESEM).

2. Materials and methods

2.1. Palm shell

Palm shell was purchased from the Seri Ulu Langat Palm Oil Mill Dengkil, Selangor, Malaysia. The palm shell was washed several times with tap water and then with distilled water to remove any dirt and impurities. The washed palm shell was dried in an oven at 105 °C for 24 h. The dried palm shell samples were ground using an aggregate crusher and separated into various size ranges using different size sieves. The ratio of the particle size was predicted to achieve the precise composition of the palm shell. The weight of every sample for each experiment was prepared based on the weight distribution percentage shown in Table 1 and was kept the same in all experiments.

Table 1
Size distribution of raw palm shell used for hydrochar production.

Size of particle (μm)	Percentage of weight distribution
$x < 500$	6.1
$500 < x < 1000$	5.5
$1000 < x < 1400$	4.8
$1400 < x < 2000$	8.9
$2000 < x < 2500$	5.9
$x > 2500$	68.8

2.2. Experimental procedure

Hydrothermal carbonization of palm shell was performed in a high-pressure stainless steel batch reactor with a volumetric capacity of 1 L. The parameters selected were temperature from 180 to 260 °C, reaction time 30–120 min and biomass to water ratio ranging from 1.10 to 1.60 by wt.%. The selection of biomass to water ratio is based on the findings from a previous study that suggested that a higher biomass to water ratio leads to lower carbonization [15]. Samples of palm shell and distilled water were mixed in the vessel of the reactor at the preset values of biomass to water ratio with maximum loading of 500 g. The reactor was closed tightly and nitrogen (N_2) gas was purged at 3 bars to ensure that the reactor was fixed tightly. After confirming that there was no leakage, the reactor was pressurized with pure N_2 gas up to 10 bars to sustain the solution's liquid phase and prevent the vaporization at elevated pressure and temperature. The temperature and stirrer speed (400 rpm) values were set accordingly in the control system, and the heater was switched on to achieve the preset temperature. After attaining the set temperature, the respective reaction time was noted. Once the preset time was achieved, the heater and stirrer were switched off and the cooling coil was started to circulate water through the joints of the reactor to cool the product to 25 ± 1 °C. The slurry of the product, including hydrochar, bio-oil, and water-soluble products, was removed manually. The gaseous products were in minor quantities and were vented. The slurry was then filtered using Fioroni filter paper, grade 601 to separate the hydrochar and bio-oil products. The recovered hydrochar was washed with distilled water a few times to remove the water-soluble products and was kept in an oven at 105 °C for 24 h. The solid product was weighed and characterized after drying.

2.3. Optimization of hydrochar production using CCD

The central composite design (CCD) of response surface methodology (RSM) was applied for optimization of the hydrochar production through hydrothermal carbonization of palm shell. The CCD was chosen to match a quadratic polynomial model with the least number of experiments as it helps to investigate the interaction between the effective parameters and also recognizes the main factor for response optimization [16]. The suggested variables and their levels are listed in Table 2. Twenty runs of experiments were suggested by the experimental design for the production of hydrochar. The response of every run was further studied by using the design expert software version 6.08 and company Stat-Ease, Inc. 2000 to look for the optimum reaction condition. The complete design matrix for the experiments and responses (yield percentage) is shown in Table 3.

2.4. Yield percentage of hydrochar

The yield percentage of hydrochar is defined as the weight of dry hydrochar to the weight of dry raw material, as shown in Eq. (1).

Table 2
Variations of bio-char production with their levels for the CCD.

Factor	Temp (A)	Time (B)	Biomass to water ratio (C)
Unit	°C	Min	wt.%
High	260	120	1.60
Low	180	30	1.10
High coded	1	1	1
Low coded	−1	−1	−1