



Research article

Examination of gas and solid products during the preparation of activated carbon using phosphoric acid



Emine Yagmur^a, I. Isil Gurten Inal^a, Yavuz Gokce^a, T. Gamze Ulusoy Ghobadi^b, Tugce Aktar^a, Zeki Aktas^{a,*}

^a Department of Chemical Engineering, Faculty of Engineering, Ankara University, Tandogan, 06100, Ankara, Turkey

^b UNAM – National Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent University, 06800, Ankara, Turkey

ARTICLE INFO

Keywords:

Waste tea
Chemical activation
Microwave pretreatment
Phosphoric acid
Activated carbon
Characterisation

ABSTRACT

Activating agents play significant roles in the preparation of activated carbon (AC) from biomasses and their wastes, which are widely used in AC production. Application methods are also important for the production process. Products give remarkable ideas regarding the method and heat treatment process. The activated carbon was produced from waste tea in accordance with either the conventional method or microwave energy pretreated method using phosphoric acid (H_3PO_4) as activating agent. The yields of the activated carbons were 51.8% for conventional method and 46.0% for microwave pretreated method. The acid suppressed the formation of tar and promoted the amount of solid and aromatic structure accordance to sp^2 hybridisation. Additionally, the waste tea was directly carbonised (without H_3PO_4) and the yield was 36.3%. Major gas (H_2 , CH_4 , C_2H_6 , C_2H_4 , CO_2 and CO) products obtained during heat treatment process in a conventional furnace were examined in terms of quantity and quality. The solid products were characterised in terms of surface area, pore size and surface properties. The result of gas analysis showed that phosphoric acid affected formation of activated carbon mechanism and significant reactions occurred during microwave pretreatment process.

1. Introduction

Lignocellulosic biomasses and their wastes are low cost potential raw materials to produce high surface area activated carbon. The cellulose, hemicellulose and lignin contents control the porosity development and surface properties of the activated carbon. The activated carbon is widely used in different fields due to its composition and renewable nature, and plays a significant role in adsorption technologies, battery electrodes, capacitors, and gas storage (Dias et al., 2007; Peláez-Cid et al., 2016; Nabais et al., 2013; Gokce and Aktas, 2014; Inal et al., 2015). A variety of lignocellulosic materials such as waste tea (Yagmur et al., 2008; Gurten et al., 2012; Fadhil et al., 2012), corn cob (Song et al., 2013), rice husk (Somasundaram et al., 2013), sugar cane bagasse (Rufford et al., 2010), palm shell (Arami-Niya et al., 2012), lignin (Gao et al., 2013), and so on have been used as precursors to produce the activated carbon. The activated carbon is prepared by physical activation in an oxidizing atmosphere (such as CO_2 , H_2O , O_2) or by chemical activation with chemical reagents such as KOH (Wu et al., 2011; González-García et al., 2013), NaOH (Foo and Hameed, 2012; Islam et al., 2017), ZnCl_2 (Zyoud et al., 2015), H_3PO_4 (Jagtoyen and Derbyshire, 1998; Yagmur et al., 2008; Gokce and Aktas, 2014) and

K_2CO_3 (Gurten et al., 2012) under different conditions. The activation temperature depends on the type of activating agent, for example, 700–900°C for KOH, NaOH and K_2CO_3 (Gao et al., 2013; Foo and Hameed, 2012; Gurten et al., 2012), 500–700°C for ZnCl_2 (Molina-Sabio and Rodriguez-Reinoso, 2004), and 400–500°C for H_3PO_4 (Jagtoyen and Derbyshire, 1998; Yagmur et al., 2008).

H_3PO_4 is widely used for the production of activated carbon from lignocellulosic materials (Jagtoyen and Derbyshire, 1998; Yagmur et al., 2008; Gokce and Aktas, 2014; Hared et al., 2007; Dobelet et al., 1999; Zuo et al., 2009). Phosphoric acid integrates in the interior of cell walls of the lignocellulosic materials during heating process. Eventually the biomass is converted into a solid product with a highly developed pore structure. The amount of solid product increases due to the crosslinking reactions (above 300°C) as results of hydrolysis and dehydration by H_3PO_4 (Jagtoyen and Derbyshire, 1998; Solum et al., 1995; Zuo et al., 2010). Jagtoyen and Derbyshire (1998) stated that phosphoric acid has two functions in the process. The first is to promote bond cleavage reactions and the creation of crosslinks by means of processes, for example cyclisation and condensation. The second is to combine with organic species to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments. Zuo et al.

* Corresponding author.

E-mail address: zaktas@eng.ankara.edu.tr (Z. Aktas).

(2012) reported that the presence of phosphoric acid noticeably depressed the evolution of CO, CO₂ and CH₄ and promoted H₂.

As reported above many studies are available in the existing literature relating to the preparation of activated carbon from lignocellulosic biomasses in the presence of phosphoric acid. In the majority of these studies, attention has been focused on the solids and their characteristics. The literature investigating both the gas and solid products at the same time during heat treatment process (Zuo et al., 2012) is very limited. Research investigating the relationship between the gas evolution and the solid product characteristics would provide significant knowledge regarding the mechanism of the process.

Microwave heating method has been recently used for the preparation of the activated carbon as well as the conventional heating processes (Yagmur et al., 2008, 2013; Yagmur, 2012; Foo and Hameed, 2012). Our previous studies (Yagmur et al., 2008) showed that microwave pretreatment enhanced surface properties (particularly total surface area increased nearly 10–24%) of the activated carbon compared to the conventional method. In this research, experiments were performed to prepare activated carbons from factory waste tea according to the conventional and microwave pretreatment methods using phosphoric acid.

The objective of the study is to examine the gas and solid products and to establish the relationship between the gas and solid products. It is also to show the effects of microwave pretreatment in the presence of phosphoric acid on the amounts and properties of gas and solid produced.

2. Experimental

2.1. Materials and material fabrication

Factory waste tea (WT, particle size: less than 500 µm) was chosen as a raw material to prepare activated carbon in the presence of phosphoric acid (Merck, 85%) which was used as an activating agent. The waste tea was collected from a tea plant located in Eastern Black Sea region in Turkey.

Three sets of experiments were performed. The first involved direct carbonisation of the raw material (WTR). The second used a conventional method where the mixture of the raw material and phosphoric acid was carbonised-activated (WTC). Unlike our previous works (Yagmur et al., 2008), a temperature programmable rotary tube furnace was used to be able to collect properly gaseous product. The third one utilised a microwave pretreatment process (WTMW). In this third case, the acid-raw material mixture was pretreated first in a domestic microwave oven and then the mixture was carbonised-activated in the same furnace as specified above. The whole process is schematically presented in Fig. 1.

Heat treatment of the samples was conducted in a quartz tube reactor placed in the furnace. Pure nitrogen gas was provided as an inert gas atmosphere and the flow rate of nitrogen was 150 ml/min. For each sample (the raw material, mixture of raw material + H₃PO₄) was heated to temperature of 450 °C at the constant heating rate (10 °C/min). The solids in the reactor were held at 450 °C for 1 h. Gaseous material was collected in Tedlar sample bags during the heat treatment process at different temperature intervals (Table 1).

The raw material (waste tea, WTR) was directly carbonised in the furnace without using any activating agent. Activated carbon was produced in two ways: conventional (WTC) and microwave pretreatment (WTMW) methods. In the conventional method (WTC), the waste tea was mixed with H₃PO₄ (85%, wt) at the acid/waste tea ratio of 2/1 (wt/wt). The mixture was loaded to the rotary tube furnace for the heat treatment process. In the microwave pretreatment method (WTMW) the mixture was directly subjected to microwave radiation for 30 s before loading the furnace (Yagmur et al., 2008). A domestic microwave oven (Vestel, MDG-620) was used for the pretreatment process. The frequency and the input power of the microwave oven were 2.45 GHz and

900 W, respectively. The microwave pretreated sample was placed in the rotary tube furnace for further activation/carbonisation process as described for the conventional method (see Fig. 1). Following treatment in the furnace in the presence of phosphoric acid, the sample was removed and mixed with hot distilled water (500 ml, 80 °C) and held in the water for 12 h and then washed and filtered. The solid fraction was dried in an oven at 110 °C overnight. The sample was then turned in a mill (IKA, M20 Universal Mill) at 20 000 rpm for 3 min, in order to liberate trapped acid. The milled sample was re-washed with distilled water until the filtrate became neutral and the solid fraction was dried for analyses.

2.2. Analyses

2.2.1. Gas analysis

The gases collected in Tedlar sample bags were analysed in a gas chromatograph (Micro GC T3000, SRA Instruments) equipped with a dual-column (MS 5A and PPU) and micro thermal conductivity detectors. The SOPRANE software package was used to identify the collected data by quantifying the peak areas. The collection temperatures of the gas samples are tabulated in Table 1. Gas analysis details and micro-GC conditions (Table S1) are reported in the Supplementary Information.

2.2.2. Solid analysis

The carbon, hydrogen, nitrogen and sulphur contents of the raw materials and the solids were analysed using a LECO CHNS 932 Elemental Analyser. The oxygen content was calculated by difference. The BET surface area and pore size distributions (the Non Local Density Functional Theory, NLDFT, method) of the samples were determined using a Quantachrome NOVA 2200 series volumetric gas adsorption instrument (Evans and Tarazona, 1984). The analysis details are presented in the Supplementary Information.

2.2.3. FTIR analysis

FTIR (Fourier Transform Infrared Spectroscopy) analyses of the solids were performed using a Shimadzu FTIR - 8040 spectrophotometer. The spectra were completed in the range of 400–4000 cm⁻¹. Thin KBr pellets have been prepared with the mass ratio of 300:1 (KBr:Sample) for the samples.

2.2.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Scientific, K-Alpha, x-ray photoelectron spectrophotometer with Al Kα x-ray source (1486.6 eV). The binding energy scales of the high resolution spectra were calibrated by shifting C1s peak position to 284.8 eV. Peak deconvolution was carried out using Gaussian-Lorentzian curves. The survey scans were obtained using the pass energy of 200 eV and a step size of 1 eV. High resolution scans were performed using a pass energy of 30 eV and a step size of 0.1 eV.

3. Results and discussion

3.1. Analysis of gases

Thermal decomposition of lignocellulosic materials (hemicellulose, cellulose and lignin) occurs at two different temperature steps; high (> 300 °C) and lower (< 300 °C) temperatures. Major noncondensable gases such as CO, CO₂, H₂, and CH₄ are released during the carbonisation process of these materials (Ronsse et al., 2015; Li et al., 2015; Ferrera-Lorenzo et al., 2014a). However, it is well known and commonly reported that phosphoric acid changes the depolymerisation and dehydration mechanisms during the heat treatment process (Jagtøyen and Derbyshire, 1993, 1998; Dobelet et al., 1999). According to Jagtøyen and Derbyshire (1998), phosphate esters form on cellulose side chains at < 450 °C in the presence of phosphoric acid. The acid is eliminated at higher temperature (> 450 °C). In this process,

Download English Version:

<https://daneshyari.com/en/article/10149075>

Download Persian Version:

<https://daneshyari.com/article/10149075>

[Daneshyari.com](https://daneshyari.com)