J. of Supercritical Fluids 95 (2014) 546–552

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Visual and Raman spectroscopic observations of hot compressed water oxidation of guaiacol in fused silica capillary reactors

Jiaojiao Jin[a], Junliang Wang[a], Yuan Shen[a], Chunmian Lin[a], Zhiyan Pan[a,*], I.-Ming Chou[b]

[a] Department of Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, P.R. China
[b] Laboratory for Experimental Study Under Deep-sea Extreme Conditions, Sanya Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya 572000, P.R. China

ARTICLE INFO

Article history:
Received 18 February 2014
Received in revised form 30 August 2014
Accepted 3 September 2014
Available online 16 September 2014

Keywords:
Guaiacol
Hot compressed water oxidation
Raman spectroscopy
Phase behavior

ABSTRACT

Using fused silica capillary reactors (FSCRs), we investigated the decomposition of guaiacol during hot compressed water oxidation (HCWO), with H_2O_2 added in stoichiometric ratios from 100 to 300%. Reactions were performed between 180 and 300 °C for durations from 2 to 10 min while the concurrent generation of CO_2 during the oxidation process was followed by Raman spectroscopy and the phase behavior of guaiacol in HCW, with or without H_2O_2, was observed visually under a polarized microscope configured with a heating/cooling stage. We found that complete conversion of guaiacol and 100% yield of CO_2 were achieved with a 150% stoichiometric ratio of oxidizer after 10 min at 200 and 300 °C, respectively. Based on the global reaction kinetics for the complete conversion of guaiacol to CO_2, the reaction is considered to be first order. The activation energy and pre-exponential factor for CO_2 formation are 18.62 kJ mol^{-1} and 12.81 s^{-1}, respectively.

1. Introduction

In recent years, the pulp and paper industry has been producing very large volumes of wastewater containing organic materials, with particularly high concentrations of lignin. Lignin is the principal constituent of plant materials, typically comprising from 16 to 33% of plant biomass. It is a heterogeneous aromatic polymer with a complex three-dimensional structure composed of methoxylated phenylpropane repeating units connected by either C—C or ether bonds [1–3]. The wastewater generated from the production of paper products is particularly difficult to process owing to the presence of lignin and this type of effluent is typically treated with biological oxidation technologies, such as two-stage anaerobic fixed bed reactor processing [4] and catalytic oxidation with Rhus laccase [5]. Several non-biological methods have also been investigated, such as the heterogeneous photo-Fenton process [6] and titanium dioxide photocatalysis [7]. However, these methods have numerous drawbacks, including inefficiency, low decomposition yields and long processing times. It is therefore necessary to find new methods for the disposal of this particular type of effluent.

Hot compressed water oxidation (HCWO) has proven to be an effective means of decomposing various organic compounds [8,9]. During this process, organics are readily degraded to numerous intermediate products which are then rapidly decomposed to smaller inorganic molecules such as H_2O and CO_2 [10]. HCWO uses an intriguing reaction medium and exhibits many extraordinary chemical and physical properties which are beneficial with regard to chemical reactions [11,12]. Since it involves nontoxic reagents and is environmentally friendly and inexpensive [13]. HCWO has been widely applied, such as in the hydrothermal conversion of biomass [14,15] and in extraction technologies used to remove various contaminants, including those resulting from dyeing [16,17]. Compared with liquid water, the diffusion coefficient and viscosity of HCW are significantly higher, the relative dielectric constant is lower [18] and the density is almost equivalent. The physical properties of HCW can also be changed dramatically by varying temperature and pressure [19] which allows HCW to be applied to numerous chemical reactions.

Guaiacol is an important intermediate in the organic synthesis of pharmaceuticals and fine chemicals and is commonly found in nature within resin, pine oil and oils resulting from the pyrolysis of hardwoods [20]. It is the building block responsible for many of the important structural features of lignin, which contains three types of C—O bonds: C—OH, C—OCH_3 and C—CH_3 [21]. In previous publications, the hydrolysis of guaiacol in supercritical water without the addition of an oxidizer (H_2O_2) has been reported [22,23]. The

---

* Corresponding author. Tel.: +86 571 88320061; fax: +86 571 88320061.
E-mail address: panzhiyan@zjut.edu.cn (Z. Pan).

http://dx.doi.org/10.1016/j.supflu.2014.09.002
0896-8446/© 2014 Elsevier B.V. All rights reserved.

main purpose of these earlier studies was to disassemble the guaiacol to form other organic compounds under conditions including relatively high temperatures. However, the complete oxidation of guaiacol using HCWO together with the addition of H_2O_2 has not yet been reported.

In this study, we used chemically resistant fused silica capillary reactors (FSCRs), instead of a traditional stainless-steel autoclave reactor. The FSCR is advantageous since it is resistant to high temperature, pressure and corrosion, and more importantly, allows in situ observations. Using FSCRs, we examined the effects of the stoichiometric ratio of the oxidizer, the temperature and the reaction time on the HCWO of guaiacol. We employed Raman spectroscopy and high-performance liquid chromatography (HPLC) to qualitatively and quantitatively analyze the gas phase products in situ and the amount of residual guaiacol after quenching of the reaction. Phase changes of the samples within the FSCRs, which were placed on a heating-cooling stage, were also observed in situ under a polarized microscope during heating and cooling. Our research group have described the experimental details previously [8,24].

Previous studies of reaction kinetics have primarily focused on the disappearance of the reactant rather than the conversion of total organic carbon to CO_2. In this study, we present our results in terms of CO_2 formation during the decomposition process and derive a reaction kinetics model based on the data. We examined the decomposition of the model compound guaiacol during HCWO within FSCRs so as to obtain information which may provide a basis for the effective treatment of papermaking wastewater.

2. Materials and methods

2.1. Materials

Reagent grade guaiacol (CAS 90-05-1, purity > 99.0%) was obtained from the Puzhen Biological Technology Co., Ltd. (Shanghai, China). The compound has a reported molecular weight of 124.13, density of 1.12 g/ml and boiling point of 205 °C and must be stored away from light. H_2O_2 (CAS 7722-84-1, 30 wt%) was used as the oxidizer and was purchased from the Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Fused silica capillary tubes (665 μm O.D. and 300 μm I.D. or 4 mm O.D. and 2 mm I.D.) were purchased from Polymicro Technologies LLC (Phoenix, AZ, USA) and Technical Glass Products, Inc. (Painesville, OH, USA), respectively.

2.2. Experimental setup and procedure

Sections of fused silica capillary tubing (about 15–25 mm long in the case of the 665 × 300 μm tubing and about 60 mm long in the case of the 4 × 2 mm tubing) were prepared in advance and one end of each tube was sealed shut in an oxyhydrogen flame. The desired amount of guaiacol was injected into each tube using a microliter syringe, after which the reaction medium (H_2O_2 or H_2O) was injected and the two immiscible liquid phases were then centrifuged to the closed end. The closed end of the tube was subsequently immersed in liquid nitrogen while the open end was sealed with an oxyhydrogen flame to form the FSCR (Fig. 1).

A heating/cooling stage system (INS0908051, INSTEC Inc., Boulder, CO, USA) was used to heat the smaller FSCRs (665 μm O.D.). A polarized microscope (DM2500P, Leica, Wetzlar, Germany) and a computer with a digital camera (TK-C1481, JVC, Yokohama, Japan) were employed to observe and record the phase changes, respectively. The larger FSCRs (4 mm O.D.) was heated inside a preheated convection oven and, after the desired reaction time, were removed from the oven and immediately immersed in a cold water bath to quench the sample to room temperature. The reaction time was defined as the time between the temperature inside the FSCR reaching 94% of the oven temperature and quenching. The experimental details have been described previously [25,26]. Three independent experimental trials were performed under each different set of conditions and the final data resulted from the averages of these measurements.

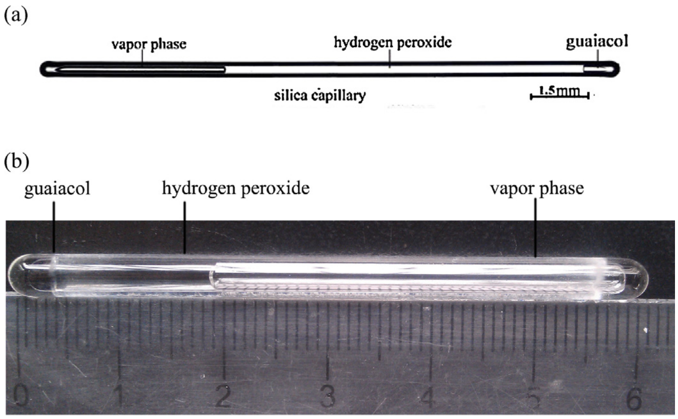

Fig. 1. Photomicrograph of fused-silica capillary reactor with reactant before reaction. (a) The smaller FSCR (665 μm O.D., 300 μm I.D.). (b) The larger FSCR (4 mm O.D., 2 mm I.D.).

2.3. Sample analysis

The amount of gaseous CO_2 generated by the decomposition of guaiacol in the HCW was determined both qualitatively and quantitatively using Raman spectroscopy, which is a non-destructive technique commonly used to characterize liquid and gaseous compounds in fluid inclusions [27]. Raman spectra were collected using a LabRam HR 800 system (Horiba Jobin-Yvon, Villeneuve d'Ascq, France) with LabSpec 5 data collection and analysis software. The instrument was equipped with a 531.95 nm, 20 mW, frequency doubled Nd:YAG He–Ne excitation laser in addition to a 600 grooves/mm grating, a multichannel, air cooled CCD detector, and a 10× long working distance Olympus (Tokyo, Japan) objective with a 0.25 numerical aperture. Spectra were collected from 1200 to 1600 cm^{-1} (covering the CO_2 Fermi diad Raman peaks) with a 90 s exposure time and 2 s accumulation time for each spectrum, applying a resolution of about 1 cm^{-1}. The FSCRs were placed directly on glass slides to collect CO_2 Raman spectra while remaining sealed.

The residual guaiacol concentration in unsealed FSCRs was determined using an HPLC instrument (Jasco LC2000, Japan) equipped with a Eclipse XDB-C8 column (4.6 mm × 250 mm × 5 μm) with methanol/water (65/35, v/v) as the mobile phase at a flow rate of 0.5 mL/min. An ultraviolet detector was employed at 254 nm and 35 °C. The guaiacol concentration in each FSCR was determined by comparison with a standard calibration curve.

The liquid phase intermediate products were determined via gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890 GC (Agilent Technologies, Santa Clara, CA, USA) with an HP-5 capillary column (30 m, 0.32 mm I.D., film thickness 0.25 μm) coupled with a mass selective detector. The oven temperature was initially held at 80 °C for 2.5 min then ramped up to 190 °C at a rate of 5 °C/min. The GC inlet and detector were set at 230 and 250 °C respectively. The distribution ratio was 10:1.