VISUAL AND RAMAN SPECTROSCOPIC OBSERVATIONS OF HOT COMPRESSED WATER OXIDATION OF GUAIACOL IN FUSED SILICA CAPILLARY REACTORS. Zhiyan Pan¹ and Jiaojiao Jin²,
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Introduction: Using fused silica capillary reactors (FSCRs), we investigated the decomposition of guaiacol during hot compressed water oxidation (HCWO), with H₂O₂ 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 CO₂ during the oxidation process was followed by Raman spectroscopy and the phase behavior of guaiacol in HCW, with or without H₂O₂, was observed visually under a polarized microscope configured with a heating/cooling stage. We found that complete conversion of guaiacol and 100% CO₂ yield 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 CO₂, the reaction is considered to be first order. The activation energy and pre-exponential factor for CO₂ formation are 18.62 kJ mol⁻¹ and 12.81 s⁻¹, respectively.

Materials and methods:
Materials: Reagent grade guaiacol (CAS 90-05-1, purity>99.0%) was obtained from the Puzhen Biological Technology Co., Ltd. (Shanghai, China). H₂O₂ (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.

Experimental setup and procedure: Sections of fused silica capillary tubing (about 15 to 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 with an oxyhydrogen flame. The desired amount of guaiacol was injected into each tube using a microliter syringe, after which the reaction medium (H₂O₂ or H₂O) 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).

Results and discussion:
Phase changes of guaiacol with H₂O₂ in an FSCR: Fig. 2 shows images of the phase behavior of guaiacol in 30 wt% H₂O₂ during heating from 25.6 to 320 °C and during cooling to ambient temperature at the rate of 10 °C/min.

Effect of the stoichiometric ratio of the oxidizer: Fig. 3 shows the effects of the stoichiometric ratio of the oxidizer on the guaiacol conversion yield, when the reaction is maintained at 165 or 185 °C for 5 min, and the amount of oxidizer is varied from 100 to 300%. It can be seen that the guaiacol conversion yield increased as the ratio was changed from 100 to 150%, but was relatively constant over the range of 150 to 300%, indicating that greater amounts of the oxidizer are helpful to the decomposition of guaiacol in the HCW owing to the increased collision frequency between oxygen and organic molecules.

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.)

Fig.2. Photomicrographs of guaiacol in smaller FSCR during heating /cooling process, with hydrogen peroxide solution (30 wt%)
Fig. 3. Effect of the stoichiometric ratio of the oxidizer (H₂O₂) on guaiacol conversion yield in larger FSCR (T = 165 °C, 185 °C, t = 5 min).

Effect of reaction temperature and time on the guaiacol conversion yield: Trials were conducted to examine the effects of reaction temperature (between 160 and 200 °C) and time (2 to 10 min) on the removal of guaiacol, with the results shown in Fig. 4. As can be seen, the general trend was that the guaiacol conversion yield increased with increasing temperature and reaction time. However, the increase in yield with time was more pronounced at higher temperatures (180-200 °C) than at lower temperatures (160 and 170 °C), which indicates that the decomposition efficiency during HCWO strongly depends on temperature and that higher temperatures are more conducive to the decomposition of guaiacol.

Fig. 4. Effect of the reaction time on guaiacol conversion yield with 150% stoichiometric ratio of the oxidizer (H₂O₂) at different temperatures in larger FSCR.

Effect of reaction temperature and time on CO₂ yield: Fig. 5 shows the effect of reaction temperature and time on the CO₂ yield from the HCWO process. These results demonstrate that the CO₂ peak area increased with increasing reaction temperature and time, eventually plateauing (peak S*, CO₂ yield=100%) at 300 °C and a reaction time of 10 min, indicating that all organic compounds had been completely transformed to CO₂ at that point.

Fig. 5(a). Raman peak area of CO₂ and CO₂ yield (lines) with 150% stoichiometric ratio of the oxidizer (H₂O₂) at the temperature range of 160-200 °C in larger FSCR.

Fig. 5(b). Raman peak area of CO₂ and CO₂ yield (lines) with 150% stoichiometric ratio of the oxidizer (H₂O₂) at the temperature range of 200-300 °C in larger FSCR.

Reaction kinetics analysis for the HCWO of guaiacol in an FSCR: The overall decomposition reaction of guaiacol to CO₂ was assumed to follow pseudo-first order kinetics, as expressed by the following equation:

\[ \ln(1-x) = -kt \]

Here x is the CO₂ yield, k is the global rate constant for CO₂ formation and t is the reaction time. Fig. 6 shows the linear relationships between t and \( \ln(1-x) \) over the temperature range of 200-280 °C, all of which have R² values above 0.98, indicating that CO₂ formation by the decomposition of guaiacol through HCWO follows first order kinetics.

Fig. 6. Linear relationships between \( \ln(1-x) \) and the reaction time for the HCWO of guaiacol.