Supercritical water oxidation of Quinazoline: Effects of conversion parameters and reaction mechanism

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Yanmeng Gong, Yang Guo[*], Shuzhong Wang, Wenhan Song

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China

ABSTRACT

The supercritical water oxidation reaction of quinazoline and a set of related reaction products were investigated in batch reactors by varying the temperature (T, 400–600 °C), time (t, 0–400 s), water density (ρ, 70.79–166.28 kg m^{-3}) and oxidation coefficient (OC, 0–4.0). The TOC removal efficiency (CRE) increased significantly as the OC increased, whereas this effect was very limited at high OC (>2.0). Lack of oxygen resulted in low CRE and TN removal efficiency (NRE), also cause coke-formation, and giving high yield of NH_3 and nitrogenous organic intermediates. Prolonging reaction time did not provide an appreciable improvement on CRE but remarkably increased NRE at temperature higher than 500 °C. Pyrimidines and pyridines as the nitrogenous intermediates were largely found in GC-MS spectrum. Polymerization among benzene, phenyl radical and benzyl radical played important roles in the formation of PAHs, such as naphthalene, biphenyl, phenanthrene. These collective results showed how the yield of intermediate products responded to changes in the process variables, which permitted the development of a potential reaction network for supercritical water oxidation of quinazoline.

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1. Introduction

Supercritical water oxidation (SCWO) has been proposed as a promising technology for complete destruction of waste that are rich in hazardous organic pollutants, such as sewage sludge, military wastes and variety of industrial wastes (Gloyna and Li, 1995). It is well known now that supercritical water (SCW, T ≥ 374 °C, P ≥ 22.1 MPa) behaves as an intermediate between its gaseous and liquid states and exhibits high diffusivity and good heat-transporting properties. The particular properties of SCW make the oxidation reaction occurring generally in a single fluid phase without transfer limitation in water/oxygen/organic mixture. In this way, the process involves a complete elimination of the target organic molecules to mainly water and carbon dioxide in SCW with excess oxygen in an extremely fast rate (Rice and Steeper, 1998). Furthermore, the low dielectric constant of SCW tremendously reduces the solubility of inorganic compounds (e.g. salts, oxides) and results in an efficient separation from water (Vadillo et al., 2013). The process is being developed as an alternative to incineration since there is virtually no formation of NO_x as a results of the relatively lower operating temperature. Besides, dioxins and other undesired incineration by-products are normally not observed in SCWO process (Bermejo and Cocero, 2006).

With the rapid development of the economy and industrialization, large amount of organic wastes are released annually into the environment from various chemical industries. Nitrogen-containing heterocyclic organic compounds with strong toxicity and chemical stability are commonly identified from wastewater in pharmacy, pesticides and chemical industries. Their widespread distribution is mainly due to their chemical inertness and poor biodegradability, making them the possible end-products which are recalcitrant to be treated properly by the conventional methods. These compounds have been studied for a long time as a possible risk to human and animal health (Battaglin and Fairchild, 2002; Belden et al., 2007). To date, some reports on SCWO of nitrogenous heterocyclic compounds have been available, such as quinoline (Pinto et al., 2006a, 2006b; Angeles-Hernandez et al., 2009) and pyridine (Aki and Abraham, 1999; Abraham and Aki, 1999; Crain et al., 1993). Pinto et al (Pinto et al., 2006a). found that SCWO is effective for treating quinoline, and the complete quinoline and TOC removal can be obtained at 575 °C and 650 °C, respectively, with the generation of CO_2 as the main gaseous product. Crain and co-workers (Crain et al., 1993) studied the SCWO

of pyridine in a temperature range of 426-525 °C with residence time varying from 2.1 to 10.7 s and O_2/pyridine molar ratio from 0 to 2.64. They proposed a reaction network for pyridine SCWO after quantitative identification of the intermediate compounds in both resultant liquid and gaseous products.

Quinazoline (Qu, $C_8H_6N_2$) and its derivatives captured our attention because of their extensive utilization in a variety of synthetic drugs, bioactive natural products, pharmaceuticals and agrochemicals and they are ubiquitous chemicals that occur widely in the environment (Kaiser et al., 2014; Kosjek et al., 2009; McDowell et al., 2005; Khan et al., 2015). Qu is a refractory N-containing condensed heterocycles made up of a benzene ring and a fused pyrimidine ring. The attention, therefore, has been particularly focused on its structure stability, toxicity and the overall destruction efficiencies, with less analysis of underlying reaction pathways and quantitative kinetics. Armarego (Armarego, 1963) introduced oxidation of quinazoline by adding potassium permanganate with large generation of pyrimidine-4,5-dicarboxylic acid. However, a complete destruction can not be achieved in this way.

To the best of our knowledge, there have been no previous reports on the oxidation reaction of quinazolines in supercritical water. This gap motivated the present investigation into SCWO reaction of Qu and their associated reaction products. In this investigation, Qu was chosen as a model compound. The effects of major operation parameters including temperature (T), water density (ρ), batch holding time (t) and oxidation coefficient on SCWO of Qu were investigated. More specifically, the targets include assessing the reactivity of Qu, quantitative analyzing of products, postulating their reaction mechanisms and developing the corresponding reaction networks. Although additional and similar reaction pathways may arise from structural differences, the results can be generalized to the respective classes of Qu.
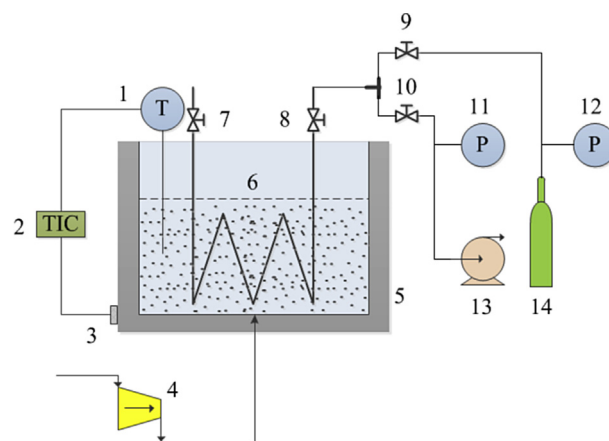
2. Experimental

2.1. Materials

Quinazoline ($C_8H_6N_2$, Purity $\geq$ 98%) used in this study was obtained from Sinopharm Chemical Reagent Company. 30 wt% H_2O_2 solution, pyrimidine, n-butyric acid, naphthalene, phenol, biphenyl (Analytical pure level) were obtained from Tianjin Jinbei Fine Chemical Reagent Company. Chromatographic grade dichloromethane used as solvent was purchased form Tianjin Comcord Technology Company.

2.2. Apparatus and experimental procedure

All experiments were performed in batch coiled tube reactors (length = 2.5 m, I.D. = 8 mm, O.D. = 14 mm), which were made of stainless steel 316. The schematic diagram of experimental setup employed in this work is demonstrated in Fig. 1. After loading quinazoline and deionized water, H_2O_2 solution was fed into each reactor in the desired amounts according to target temperature and water density. The reactors were sealed and connected them to a vacuum under 10 kPa for removal of residual air. Then the reactors were pressurized to 0.2 MPa by helium, which served as an internal standard for gas product analysis. We started the reactions when we placed the reactors into a preheated sandbath to the reaction temperature. It took about 60 to 30 s for the reactor's inside temperature achieving 400—600 °C which were measured by a portable thermocouple sheathed in a uniform-sized reactor. After the desired reaction time had elapsed, the reactors were moved out from the sandbath and immersed into cool water for at least 30 min to quench the reaction. The gaseous product was analyzed by a GC, and the liquid product was collected in test tubes for subsequent

Fig. 1. Schematic diagram of experimental apparatus. (1) thermocouple; (2) temperature controller; (3) AC power; (4) air compressor; (5) electrical heating; (6) sandbath; (7)–(10) pin valve; (11) vacuum gauge; (12) pressure meter; (13) vacuum pump; (14) helium tank.

analysis. Before each reaction, the reactors were rinsed by ethanol in order to reduce the negative effects of residual organic matter on the experimental results as much as possible.

2.3. Product analysis

The gas composition was determined by using a Beifen-Ruili GP-3420A gas chromatograph equipped with a thermal conductivity detector and a supelco 60/80 mesh Carboxen 1000 packed column. Argon served as the carrier gas. The column temperature was initially held at 120 °C for 14 min and then increased to 220 °C at a rate of 50 °C min^{-1}. The final temperature was held for 20 min, giving a total runtime of 36 min.

After openning the reactors, the collected liquid product was divided into several portions for different analysis. To prepare GC samples, organic components in liquid product was extracted by dichloromethane. Qualitative analysis of the samples was performed on an Agilent 6890 gas chromatograph and 5793 mass spectrometer equipped with a HP-5MS capillary column (30 m $\times$ 0.25 mm I.D., 0.5 μm film thickness) and using helium as the carrier gas (0.8 ml min^{-1}). The injector temperature was 300 °C. The temperature was initially held at 80 °C for 2 min and then increased to 290 °C at a rate of 6 °C min^{-1} and held for 10 min, giving a total runtime of 47 min. Another Beifen-Ruili GP-3420A equipped with a KB-Wax capillary column (30 m $\times$ 0.25 mm I.D., 0.25 μm film thickness) and a flame ionization detector was used for quantitative analysis. Helium was served as the carrier gas. The injector and detector temperature were 230 and 250 °C, respectively. The initial column temperature was held at 60 °C for 4 min and then increased to 220 °C at a rate of 10 °C min^{-1} and then held for 2 min. The amount of each compound in the sample was obtained by using linear calibrations prepared using standards of known organic matter concentrations.

The other portions were diluted with deionized water at certain ratio for different analysis on water-soluble components. The total organic content (TOC) in the sample was measured by a commercial TOC analyzer (EURO TECH, ET 1020A). We also quantitative analyzed NH_4–N, total nitrogen (TN), NO_2^- and NO_3^- spectrophotometrically based on a linear calibration which was established by using standards of known ion concentrations. Be specific, TN test was performed according to the Water quality - Determination of total nitrogen - Alkaline potassium persulfate digestion UV spectrophotometric method (Standard Method HJ 636—2012, China).