The Journal of Supercritical Fluids 138 (2018) 56–62

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Denitrification of ammonia and nitrate through supercritical water oxidation (SCWO): A study on the effect of NO_3^-/NH_4^+ ratios, catalysts and auxiliary fuels

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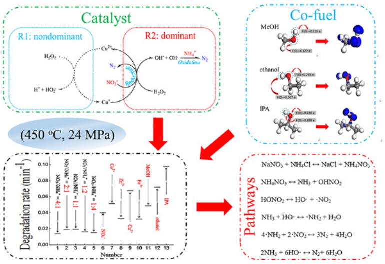
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
SCWO
Ammonia
Nitrate
Co-reaction
TN removal

ABSTRACT

Denitrification of ammonia and nitrate through SCWO has been investigated under a stable pressure of 24 MPa, temperature and reaction time of 350–550 °C and 0.5–6 min, respectively. The result showed that an appropriate ratio of NO_3^-/NH_4^+ did facilitate TN removal, which resulted in the best ratio of 1:1. The reaction of NO_2^-/NH_4^+ achieved a better TN removal than that of NO_3^-/NH_4^+. The catalysts, like Co^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+}, and co-fuels, such as methanol, ethanol and isopropyl alcohol, could play a positive role on TN removal. The results indicated that the highest degradation rate constant was found in the presence of isopropyl alcohol (IPA). The distribution of NO_3^- and NH_4^+ showed that the concentration of nitrate was much higher than that of ammonium, which revealed that the conversion of ammonia made a major contribution to TN removal.

1. Introduction

Supercritical water oxidation (SCWO) is a highly promising method for treating toxic and refractory wastes, such as wastewater, sewage sludge, biocides and waste leachate [1–3]. Above the critical point (temperature = 374 °C, pressure = 22.1 MPa), organic compounds and oxygen gas would become soluble, which could result that a rapid reaction happened within a single phase. After SCWO, most N-containing organics are promptly mineralized into CO_2, H_2O, N_2 and few inorganic salts.

Except for N_2, ammonium and nitrate are the main products from N-containing compounds after SCWO process. Lee and Park studied nitrobenzene in SCWO, and demonstrated that the decomposition of nitrobenzene firstly underwent C—N bond breaking to generate benzene, and then the decline of NO_3^- and NH_4^+ was corresponded to the increase of nitrogen gas. Furthermore, the amount of nitrate and ammonia did not change with retention time prolonging [4]. Li and Oshima examined SCWO of methylamine and found that N_2 and NH_4^+ were the main products, and the yields of ammonium would reduce through enhancing temperature or retention time [5]. Gong et al.

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https://doi.org/10.1016/j.supflu.2018.03.021
Received 4 January 2018; Received in revised form 14 March 2018; Accepted 22 March 2018

investigated quinazoline in SCW and obtained low TOC removal efficiency as well as high concentration of ammonium [6]. Similarly, Pinto et al. explored SCWO of quinoline, the results manifested that NH_4^+ was occurred in all samples as temperature and pressure ranged from 450 to 650 °C and 50–300 bar, respectively [7]. In addition, Guo et al. revealed the reaction pathway of indole in supercritical water gasification conditions, and achieved that NH_3 was the predominant N-containing product at temperature of 550–700 °C within 80 min [8].

In order to remove ammonium via sub- and supercritical water oxidation, Segond et al. used two isothermal, isobaric plug flow reactors with different surface-to-volume ratios, and found that ammonium would be primarily oxidized to N_2, NO_x and NO_3^- under reactor wall catalysis [9]. Taro et al. investigated the role of methanol (MeOH) in SCWO of ammonium, and resulted that MeOH did play a significant part in the conversion of ammonium to nitrate [10]. This result was also in agreement with those of Shimoda et al., who explored the kinetic analysis of ammonia/MeOH in SCWO, and achieved that NH_4^+ conversion would improve by the presence of MeOH, but this conversion highly declined after the completion of MeOH co-oxidation [11]. It is necessary to point out that except for N_2, the presence of NO_3^- and NH_4^+ would contribute to total nitrogen (TN) which potentially led to aggravate eutrophication in receiving water. As a result, it is significant to study the co-reaction of NO_3^- and NH_4^+ on TN removal and N conversion mechanism in supercritical water. Additionally, density functional theory (DFT) method has been widely used to explore the chemical reaction mechanism in organic structure and has successfully illuminated some experimental phenomena [12,13]. In our previous works, we found that some molecular descriptors based on DFT, like dipole moment and Fukui indices, could greatly affect temperature behavior of TOC and TN removal during SCWO [14,15].

To our best knowledge, however, there is still sparse data on particular investigation of co-reaction of NO_3^- and NH_4^+ during SCWO. Therefore, this work aims to study the potential removal of NO_3^- and NH_4^+ after SCWO process. Bench scale experiments were conducted to examine the effect of: (1) NO_3^-/NH_4^+ ratios, (2) homogeneous catalysts, (3) different auxiliary fuels. Based on these consequences, the proposal reaction pathways of NO_3^- and NH_4^+ during SCWO were presented.

2. Experimental

2.1. Apparatus and experimental procedures

The SCWO schematic diagram was shown in Fig. 1. It has been successfully applied into our previous study [15]. In brief, the continuous tubular reactor is made of Hastelloy alloy with an approximately effective volume of 10 mL. It is generally believed that SCWO reactions were effective when temperature and pressure are at 400–450 °C and 22–26 MPa, respectively, which has been successfully implemented in the present reports [16,17]. In this work, therefore, all experiments were carried out at a constant pressure of 24 MPa. Nevertheless, sampling reaction time and temperature were designed as 0.5, 1, 1.5, 3 and 6 min, as well as 350, 400, 450, 500 and 550 °C, respectively. Furthermore, the ratio values of NO_3^-/NH_4^+ were set as 0.25, 0.5, 1, 2 and 4. In order to avoid causing problematic corrosion and precipitation, the initial concentration of all the mixed was totally 1 mM.

2.2. Materials and analytical methods

$NaNO_3$, NH_4Cl, $Co(NO_3)_2$, $NaNO_2$, $Zn(NO_3)_2$, $Cu(NO_3)_2$ and $Fe(NO_3)_3$ as well as MeOH, ethanol and isopropyl alcohol (IPA) were selected as target compounds, catalysts and auxiliary fuels. H_2O_2 (30 wt%) was used in SCWO experiments as the oxidant and all reagents were analytic grade which purchased from Sinopharm Chemical Reagent Co., Ltd.

Molecular structures and properties of MeOH, ethanol and IPA were calculated by the Density Functional Theory (DFT) method using Material Studio 6.1 (Dmol3/GGA-BLYP/DNP(3.5) basis). Fukui indices could predict site reactive selectively between the reaction pathways, as hydrogen substitution by radicals attack. Therefore, the calculations of Fukui indices were adopted and carried out in Dmol3 code in Material Studio 6.1. The method was successfully conducted into the previous researches [18–20].

Measurement of total nitrogen (TN), NH_4^+, NO_2^- and NO_3^- concentration was using a photometer (Model Spectroquant® NOVA 60, Merck Limited). Gas samples, like N_2, were analyzed by GC-TCD (Agilent Technologies 6890 N) with Alltech CTR 1 column. Total organic carbon (TOC) was measured by the TOC Analyzer multi N/C 3000 (ChD).

3. Results and discussion

The concentration of nitrite was very little or even negligible from most of samples. Additionally, NO_X, like N_2O, NO and NO_2, was not detected in gas samples. Due to low concentration of NO_3^-/NH_4^+ in feed solution was applied into this study, NOx would immediately react with H_2O and form NO_2^- or NO_3^-. It is generally believed that NO_2^- was the product from incomplete oxidation reaction. Similar results were found in the study by Segond et al., they investigated SCWO of 2,4-dinitrophenol with oxygen excess of 34%, and resulted that the concentration of NO_2^- was frequently below the detection limit ($0.1\ mg\ L^{-1}$) [9].

3.1. Effect of oxidant dose

In order to explore the effect of oxidant dose, the H_2O_2 concentration was designed as 0, 1, 3, 5 and 7 mM, namely stoichiometric oxygen was 0, 100%, 300%, 500% 700%, and added into the co-reaction of NO_3^-/NH_4^+ (1 mM, 1:1, by moles). The experimental conditions were

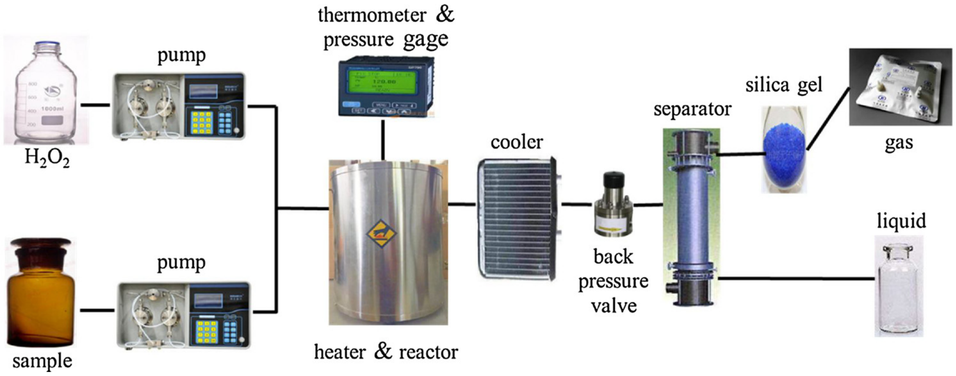

Fig. 1. Scheme of SCWO equipment.