

Hydrothermal decomposition and oxidation of *p*-nitroaniline in supercritical water

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Abstract

The decomposition kinetics and nitrogen speciation of *p*-nitroaniline (pNA) were investigated at supercritical water conditions in the absence/presence of oxygen. A tubular flow reactor system was used at the temperature ranges 385–440°C and 380–420°C for hydrothermal (oxygen absent) and oxidation experiments, respectively. The destruction of pNA significantly occurred in the absence of oxygen. The hydrothermal decomposition rate had an activation energy of $(1.59 \pm 0.25) \times 10^5$ J/mol and was first-order with pNA. The formation of oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂), and nitrogen (N₂) indicated that the nitro group in the decomposed pNA drove oxidation in the absence of oxygen. Appreciable quantity of ammonia and traces of nitrite and nitrate were formed. Oxygen enhanced the pNA destruction, although its effect did not show explicitly in the oxidation rate expression. The activation energy of the oxidation was $(1.28 \pm 0.35) \times 10^5$ J/mol. Also, in the presence of oxygen, ammonia was formed only in trace quantities. The reduction of ammonia level was attributable to the potential ammonia oxidation by the nitro group of the decomposed pNA. It follows from this result that nitro group-containing compounds may be cooxidized with other nitrogen containing substances to reduce the production of ammonia, nitrite and nitrate in supercritical water oxidation processes. © 1997 Elsevier Science B.V.

Keywords: *p*-nitroaniline; Supercritical water; Fate of nitrogen

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1. Introduction

The destruction capability of supercritical water oxidation (SCWO) has been shown by several works [1–4], in which the selected model compounds have been limited mostly to halogenated organic compounds. As there exist many problematic organic pollutants that contain heteroatoms other than halogens, expanding knowledge of destruction performance for these substances is critical to more comprehensive uses of SCWO process. As noted in a previous study [5], the destruction of nitrogen (N)-containing compounds by SCWO is of particular concern in two respects. First, some N-containing compounds appear to be fairly refractory [6–12], which require extreme SCWO conditions to accomplish high destruction efficiencies. However, there are also certain N-containing organics that are very susceptible to SCWO [12,13]. The varying degree of resistance among the N-containing substances should be sufficiently investigated for optimum design of SCWO. Second, depending upon its initial state, organic nitrogen is converted to ammonia, nitrite and nitrate [1,5,12,13], which, in certain concentrations, require additional treatments. Therefore, nitrogen speciation in SCWO conditions should be understood to minimize the additional treatment requirement.

As a continuing effort to extend the understanding of the destruction behavior of N-containing substances in SCWO environments, *p*-nitroaniline (pNA) was selected in the present work for the investigation of the destruction kinetics and nitrogen speciation. Since the SCWO of aniline and nitrobenzene, respectively, produced ammonia [12] and nitrite [5] as the main nitrogen products, and since nitrite or nitrate was an efficient oxidant for ammonia in SCWO [14], it was hoped that both the levels of ammonia and the nitrite could substantially be reduced via a possible redox process between nitro and amine groups of pNA.

2. Experimental methods

2.1. Reactor system

A tubular flow reactor system (Fig. 1) was used to conduct the experiments. The pNA feed solution was prepared in distilled–deionized water that was deoxygenated by purging He gas. The head space in the pNA feed tank was pressurized with He gas to prevent air from intrusion. For the hydrothermal experiments, only this pNA feed was used. For the oxidation of pNA, an oxygen saturator was also used in which oxygen was quantitatively dissolved in distilled–deionized water by regulating the head space oxygen pressure. The system temperature and pressure were raised while distilled–deionized water was flowing through the system. When the temperature and pressure were stable at desired levels, the water was switched to the pNA and the oxygen feed solutions. The feed solutions were separately pumped into the reactor by using two high-pressure metering pumps (ICI, LC1500; Milton Roy, Duplex). The feed solutions were preheated to reaction temperature in the preheater and were mixed at the inlet of the coiled tubular reactor that was made of ss316 tubing with 1.44 mm I.D. to have a 2.5 ml internal volume. The reaction temperature was controlled within 3°C deviation by

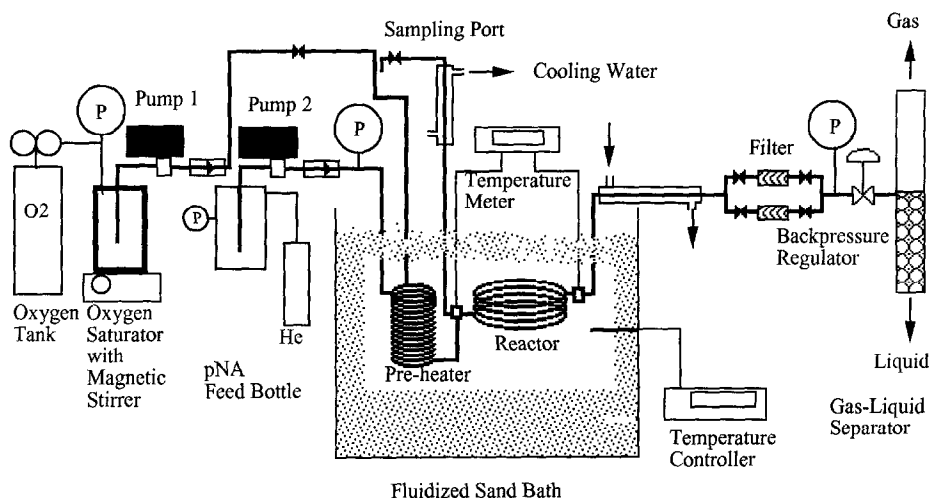


Fig. 1. Tubular reactor system for pNA reaction in supercritical water.

using heating tapes and a fluidized sandbath (Techne, SBL-2) equipped with a temperature controller. The reaction temperature was continuously monitored by using two K-type thermocouples at the inlet and outlet of the reactor. A tube- and shell-type heat exchanger followed to quench the effluent to ambient temperature. Reaction pressure was controlled by using a back pressure regulator (Autoclave Eng., 10VRMN) and measured by using a Heise gauge (CMM104951). The effluent was split into a gaseous and an aqueous phases in a gas-liquid separator. After a sufficient equilibration time (typically greater than 30 min), the aqueous phase was collected in glass vials for subsequent analyses. The gas phase effluent was connected to a gas chromatograph for online analyses.

2.2. Analytical methods

The concentration of pNA in the aqueous phase was determined by using the gas chromatograph (gc) (Younglin, GC680D) equipped with a flame ionization detector and a widebore capillary column (Supelco, SPB-5, 15 m × 0.53 mm I.D., 1.5 μm film thickness). The same gc was used for the gas phase analysis. A packed column (Supelco, Carboxen 1000) and a thermal conductivity detector were used for the separation and detection, respectively, of carbon monoxide (CO), carbon dioxide (CO₂), nitrogen (N₂), and oxygen (O₂). Quantitative determination of nitrite (NO₂⁻) and nitrate (NO₃⁻) ions was performed by using a high pressure liquid chromatograph (Waters) equipped with a photodiode array detector (Waters, PDA996) and an anion column (Waters, IC-Pak). An ammonia specific electrode with a pH/ISE meter was used to measure the aqueous phase ammonia concentration.

Identification of decomposition products in the aqueous phase was accomplished by using a gc (Hewlett-Packard, HP5890)/msd (HP5970). The aqueous phase samples

were extracted with dichloromethane in a 5:1 volume ratio and the dichloromethane phase was used for the gc/msd analysis.

3. Results and discussion

3.1. Hydrothermal decomposition in the absence of oxygen

The hydrothermal decomposition kinetics was described by using a power-law rate expression ($-r = k[\text{pNA}]^m[\text{H}_2\text{O}]^n$). The pNA dependency as represented by the reaction order m was investigated by varying the influent concentration of pNA from 3.7×10^{-5} to 5.42×10^{-4} mol/l at a fixed water density of 0.34 g/ml. Since supercritical water (SCW) is in great excess and at a constant density,

$$-r = k[\text{pNA}]^m[\text{H}_2\text{O}]^n = k'[\text{pNA}] \quad (k' = k[\text{H}_2\text{O}]^n),$$

where $[\text{pNA}]$ and $[\text{H}_2\text{O}]$ denote mole concentrations of pNA and water, respectively, at reaction conditions. A pNA mass balance in a plug flow reactor gives,

$$\int (-1/r) d[\text{pNA}] = \tau,$$

where τ is a residence time. Rearranging this equation about the conversion of pNA yields the equation:

$$X = 1 - \left\{ 1 - k'\tau(1-m)[\text{pNA}]_{\text{in}}^{m-1} \right\}^{1/1-m} \quad (m \neq 1)$$

or

$$X = 1 - \exp(-k'\tau) \quad (m = 1),$$

where X and $[\text{pNA}]_{\text{in}}$ are the conversion of and the influent concentration of pNA, respectively. As shown in Fig. 2, the experimental results indicated that the effect of

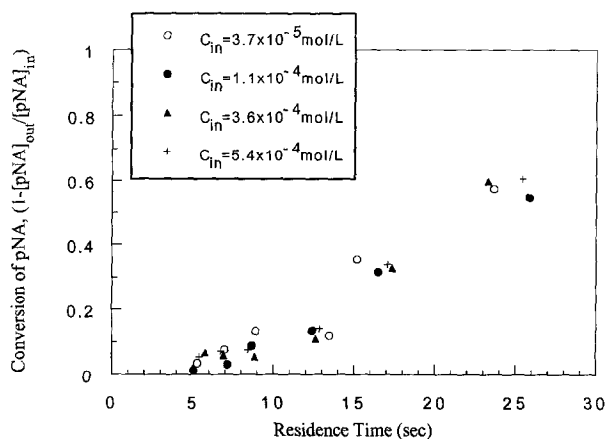


Fig. 2. Effect of influent pNA concentration on hydrothermal conversion of pNA is negligible at 400°C ($D_{\text{SCW}} = 0.34$ g/ml).

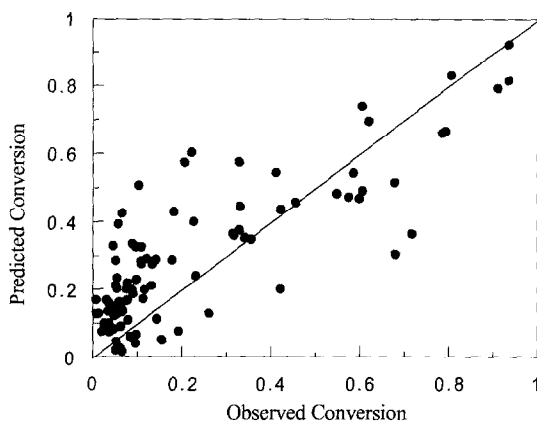


Fig. 3. Observed conversions are compared with conversions predicted by first-order rate equation with pNA.

influent pNA concentration was insignificant on the conversion. A nonlinear regression analysis using SAS confirmed that the reaction order, m , was statistically one (0.97 ± 0.19 at 95% confidence limit).

The temperature effect and the dependency on SCW were investigated by applying the simple first-order rate expression, $-r = k'[\text{pNA}]$, where $k' = k_0 \exp(-E_a/RT)[\text{H}_2\text{O}]^n$, k_0 = preexponential factor, E_a = activation energy, R = universal gas constant, and T = absolute temperature. These kinetic parameters were determined from a total of 96 tests at SCW density varying from 0.24 to 0.41 g/ml and temperature from 385 to 440°C. A nonlinear regression resulted that the reaction order with SCW, n , could statistically be -1 or zero (-0.89 ± 0.94 at 95% confidence limit). Zero order with SCW, however, resulted slight better conversion predictions as represented by the sum of squares of errors. With zero order in SCW, the preexponential factor and the activation energy were $(6.2 \pm 1.1) \times 10^{10} \text{ s}^{-1}$ and $(1.59 \pm 0.25) \times 10^5 \text{ J/mol}$, respectively. The power-law rate equation for the hydrothermal decomposition of pNA is summarized as

$$-r = (6.2 \pm 1.1) \times 10^{10} \exp(-19200 \pm 2980/T)[\text{pNA}]$$

As shown in Fig. 3, this rate equation had a tendency to overpredict the conversions less than 0.2. The tendency appeared to be due to the presence of induction periods as more apparently shown later in the oxidation results. Also, enforcing simple reaction orders of one and zero with pNA and SCW, respectively, apparently worsened the model fit.

3.2. Supercritical water oxidation

In the presence of oxygen, the oxidation and the hydrothermal decomposition of pNA would occur simultaneously. Since the two reactions are likely to affect each other, an isolation of the pure oxidation would not be possible. Therefore, the oxidation in this work refers to an apparent reaction observed as a result of the two reactions.

Thirty oxidation tests were conducted at 400°C to investigate the effect of oxygen. The initial oxygen level was varied from 0.0065 to 0.0295 mol/l at a fixed initial pNA

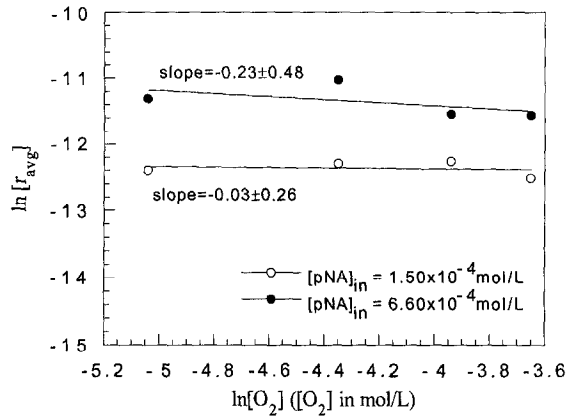


Fig. 4. SCWO rate of pNA is statistically independent of oxygen at 400°C ($D_{SCW} = 0.34$ g/ml).

concentration between 1.5×10^{-4} and 6.6×10^{-4} mol/l. As typically shown in Fig. 4, the initial oxygen level appeared to have little effect on the average rate ($-r_{avg} = ([pNA]_o - [pNA]_f)/\tau$, r_{avg} : the average rate, $[pNA]_f$: effluent pNA concentration), which suggested that the reaction order with oxygen was zero. Additional 106 oxidation tests were conducted at temperature and SCW density from 380 to 420°C and from 0.25 to 0.41 g/ml, respectively. Typical time profiles of the conversion are presented in Fig. 5. Notably, induction times of a few seconds existed as varied by the reaction temperature. The presence of an induction time is typical of free radical reactions and was observed in a previous SCWO study [15]. A nonlinear regression analysis enforcing zero-order with oxygen yielded the oxidation rate equation as

$$-r = (3.3 \pm 9.1) \times 10^8 \exp(-16000 \pm 4600/T) \times [pNA]^{0.76 \pm 0.14} [H_2O]^{-0.53 \pm 0.84},$$

where the error ranges denote 95% confidence limits. In the regression analysis, the

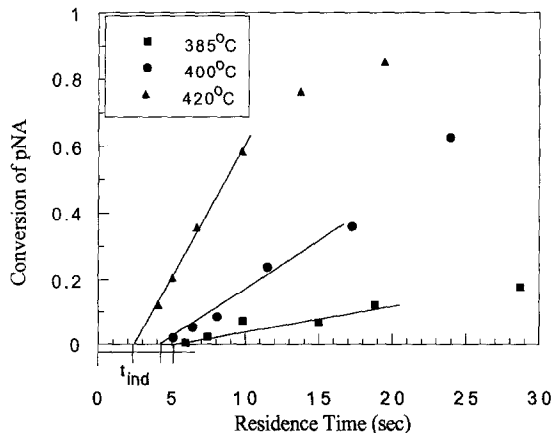


Fig. 5. Typical residence time profiles of pNA conversion exhibit a presence of induction time at SCWO conditions.

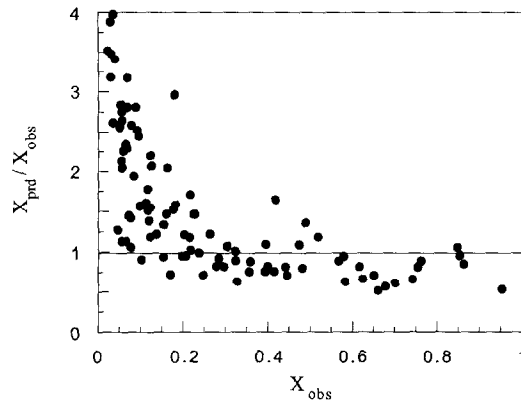


Fig. 6. The best-fit rate equation for SCWO of pNA substantially overpredicts at low conversion range when the induction time is ignored.

induction period was not considered. In Fig. 6, the ratio of the conversion predicted by this rate equation to the observed conversion was plotted against the corresponding observed conversion. Overpredictions were definitely seen at the conversions lower than about 0.2, which mostly occurred at short residence times. At a short residence time, a relatively large portion of the residence time would serve as the induction period during which little reaction took place. Therefore, the overprediction by the rate equation reflected the presence and influence of the induction period. Subtracting typically observed induction periods (5, 4, and 2 s at 380, 400, and 420°C, respectively) from the residence time yielded a new rate equation as

$$-r = (1.3 \pm 3.4) \times 10^9 \exp(-15400 \pm 4300/T) [\text{pNA}]^{0.85 \pm 0.10} [\text{H}_2\text{O}]^{-0.91 \pm 0.78}$$

This rate equation substantially reduced the overpredicting tendency to fit the conversion reasonably well as shown in Fig. 7.

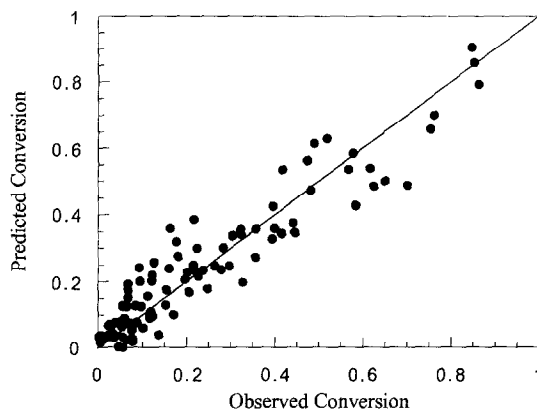


Fig. 7. Incorporating the induction time into the rate equation reduces the overpredicting problem to improve the pNA conversion fit.

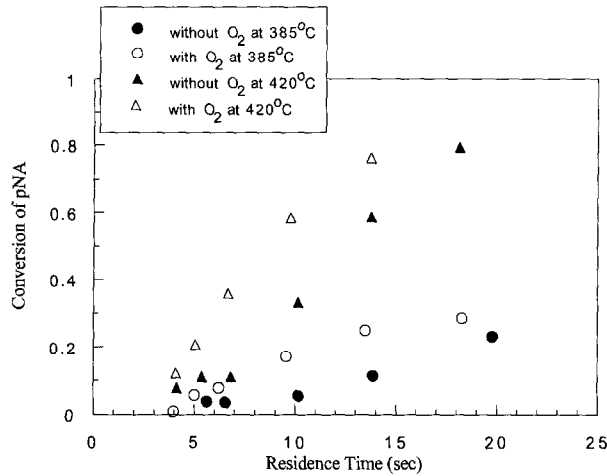


Fig. 8. Oxygen enhances the pNA conversion in SCW ($D_{SCW} = 0.25$ g/ml).

As compared in Fig. 8, the pNA conversion was enhanced in the presence of oxygen, although the effect of oxygen did not explicitly show in the rate equation. The similar effect of oxygen was observed in the SCWO of CO [9]. It was also shown in Fig. 8 that more than half of any observed conversion might occur via hydrothermal decomposition, indicating that it was a significant destruction path of pNA during the oxidation.

3.3. Nitrogen speciation

Aqueous phase analyses indicated that the hydrothermal decomposition of pNA transformed nitrogen from the amine group in the decomposed pNA mainly to ammonia. A typical ammonia formation is shown in Fig. 9. The ammonia nitrogen was equivalent to 30–70% of nitrogen from the amine group in the decomposed pNA. It was reported that SCWO of aniline predominantly produced ammonia [12]. Also, nitrobenzene

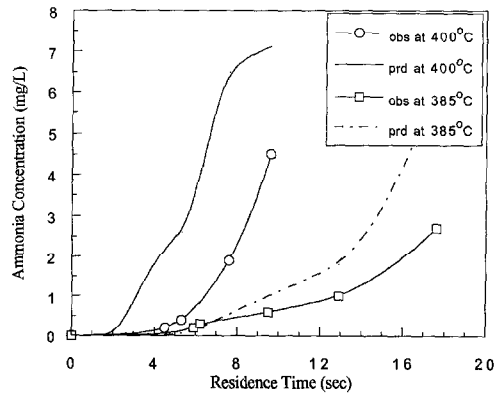


Fig. 9. Ammonia forms in less quantity than predicted based on the quantity of NH_2 from the decomposed pNA.

decomposition in SCW in the absence of oxygen produced mainly nitrite ion that was certainly formed from the nitro group of the decomposed nitrobenzene [5]. By comparison, the pNA decomposition would yield ammonia and nitrite ion as the main inorganic nitrogen species of comparable quantity. However, only trace quantity of nitrite ion (and nitrate ion) was detected in the present work. The substantially reduced concentration of nitrite ion might result from a participation of nitrogen of the nitro group to the oxidation of both ammonia (or nitrogen in amine group) and organic substances including pNA and possibly pNA decomposition products. The detection of nitrogen gas, carbon monoxide, and carbon dioxide in the gas phase effluent strongly supported the oxidative role of nitrogen from the nitro group. Besides, the role of nitrogen of the nitro group or nitrite as an electron acceptor in SCW for ammonia and some organics was previously observed [5,14]. The redox process between ammonia and nitro group appeared to yield primarily nitrogen gas (N_2) as observed in the present and previous works [5]. Also, a thermodynamic consideration predicted the formation of N_2 [16]. Nitrogen mass balance was not checked in the present work due to extremely low flows of the gas phase effluent. However, except the small portions contained in the pNA decomposition products such as aniline and 5-methyl-2-pyridineamine, it was concluded that a significant portion of nitrogen from the amine group in the decomposed pNA formed ammonia and the balance nitrogen from the amine and nitro groups mainly took the form of N_2 .

In contrast to the hydrothermal decomposition, SCWO of pNA yielded trace amounts of ammonia as well as nitrite and nitrate ions. The sum of these three species in the aqueous phase typically contributed less than 3% of nitrogen from the decomposed pNA. As in the hydrothermal decomposition, N_2 , O_2 , CO and CO_2 were found in the gas phase effluent. Considering that ammonia was formed in much more appreciable quantity in the absence of oxygen, and that oxygen was not an effective oxidant for ammonia at the temperature range of the present work [17], the coexistence of nitro group and oxygen appeared to have a synergistic effect on reducing ammonia concentration. One probable explanation for such effect was that, since oxygen could be consumed as an efficient oxidant for organic substances including pNA (as shown in Fig. 8) and its decomposition products, more nitro group should become available for the ammonia (or amine group) oxidation. Besides some inorganic forms of nitrogen such as nitrite or nitrate [14], the result of the present work demonstrates that an organic form of nitrogen (nitro group of pNA) may also be used to reduce the ammonia yield in SCWO.

4. Conclusion

In the absence of oxygen, destruction of pNA in SCW significantly took place via hydrothermal decomposition. The formation of O_2 , CO, CO_2 , and N_2 indicated that nitrogen from the nitro group of pNA drove oxidation in the absence of oxygen. In the presence of oxygen, the pNA destruction was enhanced while the ammonia production was substantially reduced. The reduced ammonia production was attributable to the potential oxidative role of the nitro group in the presence of oxygen. A cooxidation of

nitro group-containing compounds with other nitrogen containing substances might intentionally be used to limit the yields of ammonia, nitrite, and nitrate in SCWO processes.

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