

Decomposition of nitrobenzene in supercritical water

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Abstract

This work was conducted to extend the understanding of the reaction kinetics and mechanisms of nitrogen containing compounds in SCW. The main objectives were to investigate the reaction kinetics and pathways for the decomposition of nitrobenzene in SCW, and the fate of nitrogen upon the decomposition.

The experimental conditions included the temperature range from 440 to 550°C and the supercritical water density range from 0.09 to 0.23 g ml⁻¹. A continuous flow stirred tank reactor system and a batch reactor system were used for the decomposition experiments without and with oxygen, respectively.

In the absence of oxygen, nitrobenzene decomposed in SCW to form primarily benzene and nitrite. The decomposition kinetics had an activation energy of 68.0 ± 9.0 kJ mol⁻¹. Nitrobenzene concentration showed a weak effect on the decomposition kinetics whereas the density of SCW had no effect. Additional decomposition products such as carbon monoxide and carbon dioxide suggested the occurrence of oxidation driven possibly by the nitro-group as well as SCW. The oxidative role of the nitro-group was supported by the observation of the reduction of nitrite to nitrogen gas.

The decomposition rate was substantially enhanced in the presence of oxygen. The oxidation yielded a number of aromatic reaction products including aniline, phenol, 2-(2-pyridinyl)-benzo-nitrile, and dibenzofuran. The nitrogen in the decomposed nitrobenzene appeared to form mainly nitrogen gas even in the oxidative environments.

Keywords: Supercritical water; Nitrobenzene; Kinetics; Byproducts

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1. Introduction

Supercritical water oxidation (SCWO) is a promising waste treatment process that can efficiently destroy hazardous organic substances. The early SCWO works have demonstrated that high destruction efficiencies could be achieved for a wide variety of organic compounds [1–4]. As the destruction capability of SCWO has been demonstrated by these early works, more emphasis has been put to the investigation of the detailed kinetics and mechanistic aspects in later works [5–13]. Simple hydrocarbons or oxygenated hydrocarbons have been investigated in the kinetics and mechanistic works.

As many important organic pollutants contain heteroatoms such as halogens, nitrogen, sulfur and phosphorus, it is essential to extend the understanding of the reaction kinetics and mechanisms of the heteroatom-containing compounds in supercritical water (SCW). Nitrogen-containing organic compounds, in particular, are of much interest in two respects. Firstly, nitrogen from the decomposed parent compounds can take several forms depending upon its oxidation state, which may pose an additional pollution problem. Secondly, nitrogen-containing aromatic compounds appear to be fairly refractory at SCWO conditions [14–16], hence, may require more stringent conditions to achieve a high destruction efficiency. Therefore, the knowledge of kinetics and mechanisms of SCWO of such compounds is of critical design importance. However, the investigation on reaction kinetics and mechanisms of such compounds in SCW is scarce. An early study reported that SCW had a profound effect on the reaction kinetics and mechanisms of quinoline, isoquinoline, benzonitrile, carbazole and aniline [17,18]. Also, destruction kinetics of simple compounds, such as ammonia and urea, has been reported [1,10]. The fate of nitrogen was thermodynamically predicted and experimentally confirmed [19]. Kinetics and mechanisms for the hydrolysis and oxidation of acetamide in SCW were investigated [16]. The hydrolysis was the predominant destruction process for acetamide. More recently, kinetics and oxidation pathways of pyridine in SCW were reported [20]. Pyridine was found to be highly refractory. The oxidation kinetics were observed to have first order and 0.2 order dependencies on SCW and oxygen, respectively. Also, the presumed oxidation pathways were suggested based on a number of transition products identified in the gas and liquid effluents.

The present work was conducted to extend the understanding of the reaction kinetics and mechanisms of nitrobenzene in SCW. More specifically, the main objectives were to investigate the reaction kinetics and pathways for the decomposition of nitrobenzene in SCW, and the fate of nitrogen after the decomposition.

2. Experimental method

2.1. Reactor system

A continuous flow stirred tank reactor system (CFSTR) was used to investigate the decomposition of nitrobenzene in the absence of oxygen. A schematic of the CFSTR system is shown in Fig. 1. The nitrobenzene feed solution was prepared in deionized distilled water which was deoxygenated by He gas. The feed solution was pumped by a

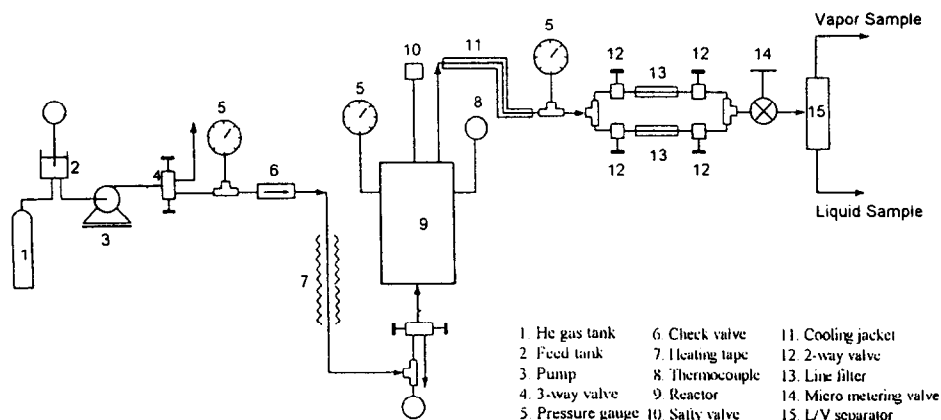


Fig. 1. CFSTR system for nitrobenzene decomposition in SCW.

high pressure pump (Milton Roy, MBIM 32PO51) into the reactor vessel (Autoclave Engineers, AE00-50AS29). The reactor vessel was made of stainless steel 316 and had a free volume of 545 ml. An anchor-type impeller was used to stir the reaction mixture in the vessel. The impeller was driven by an external stator magnet. The temperature in the vessel was controlled within $\pm 2^\circ\text{C}$ from a desired temperature by a PID temperature controller (Eurotherm, 808/TI/NO/RI/QS/AKMC-205). The reaction temperature was measured and continuously recorded by using a K-type thermocouple. The pressure was controlled by a back pressure regulator and was measured by a Heise gauge (CMM104951) and a digital gauge (Precise Sensors, CA1016). The effluent was split into the gas phase and the aqueous phase. The gas phase effluent was connected to a gas chromatograph (Hewlett-Packard 5890A) for the on-line analysis. The aqueous phase was collected in the glass sampling vial for subsequent analysis.

A batch reactor system was used for the oxidation experiments of nitrobenzene. The batch reactor system was exactly the same as the one described elsewhere in detail [21].

2.2. Analytical methods

Nitrobenzene and benzene in aqueous phase were analyzed by using the gas chromatograph (gc) equipped with an flame ionization detector (Hewlett-Packard 5890A) and an autosampler (Hewlett-Packard 7673). For the separation of these compounds, a widebore fused capillary column (Supelco, SPB-5) was used. The same gc was used for the gas phase analysis. A packed column (Carboxen 1000) and a thermal conductivity detector, respectively, were used for the separation and detection of carbon monoxide, carbon dioxide, nitrogen gas and oxygen gas. Quantification of ammonia, nitrite (NO_2^-), and nitrate (NO_3^-) concentrations were performed by using the ion chromatograph (Dionex, DX-300) with an autosampler (Spectraphysics, AS3500).

Identification of the reaction products was accomplished by using gc (Hewlett-Packard 5890)/msd (HP 5970). Prior to the analysis, the aqueous samples were extracted with dichloromethane in a 5:1 volume ratio. The dichloromethane phase was then used in the

analysis. The electron impact mode was employed. The gc retention times of the products identified by the gc/msd analysis were reconfirmed by using the authentic compounds except for dibenzofuran which was unavailable at the time of this work.

3. Results and discussion

3.1. Decomposition kinetics of nitrobenzene

The variables that were investigated in the decomposition kinetics study included nitrobenzene concentration, supercritical water density, reaction temperature, and retention time.

Preliminary experiments were conducted to evaluate the dependency of the decomposition rate on the reactants, that is, nitrobenzene and supercritical water. The nitrobenzene dependency was investigated by varying the initial concentration of nitrobenzene from $2.6 \times 10^{-4} \text{ mol l}^{-1}$ to $1.96 \times 10^{-3} \text{ mol l}^{-1}$ at 440°C and at the fixed water density of 0.16 g ml^{-1} . As shown in Fig. 2, the initial concentration of nitrobenzene apparently affected the decomposition rate. Similarly, the effect of supercritical water density was investigated by varying the density from 0.13 to 0.23 g ml^{-1} at 440°C . In a power law rate expression ($r = k [\text{C}_6\text{H}_5\text{NO}_2]_{\text{out}}^m [\text{H}_2\text{O}]^n$), the water density effect as represented by n could be determined from the following relationship:

$$\ln r - m \ln [\text{C}_6\text{H}_5\text{NO}_2]_{\text{out}} = n \ln [\text{H}_2\text{O}] + \ln k$$

where $[\text{C}_6\text{H}_5\text{NO}_2]_{\text{out}}$, k , m and n are the effluent nitrobenzene concentration, rate constant and reaction orders, respectively. The reaction order with nitrobenzene (m), however, was determined before n was evaluated. Since water was in great excess,

$$\ln r = m \ln [\text{C}_6\text{H}_5\text{NO}_2]_{\text{out}} + \ln k' \quad (k' = k[\text{H}_2\text{O}]^n)$$

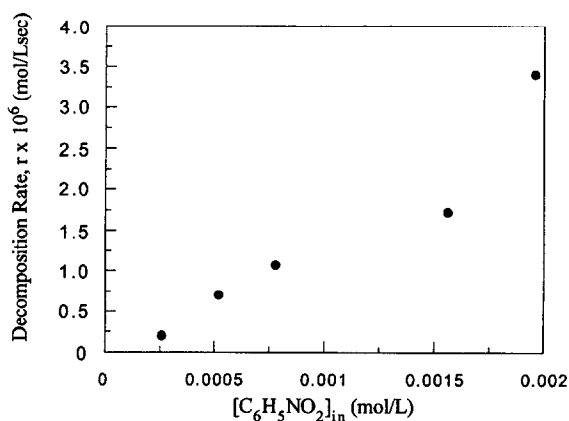


Fig. 2. Effect of initial nitrobenzene concentration on decomposition rate ($T = 440^\circ\text{C}$, $D_{\text{scw}} = 0.16 \text{ g ml}^{-1}$, retention time = 144s).

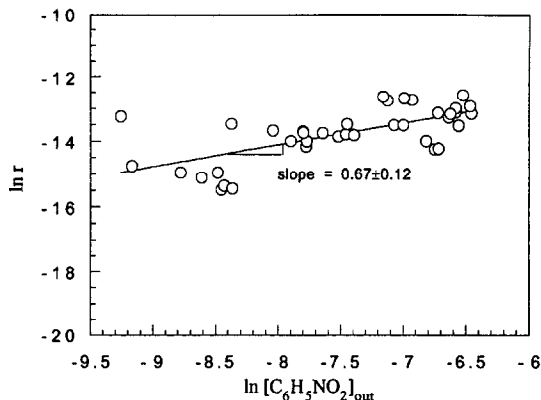


Fig. 3. Determination of reaction order with nitrobenzene at 440°C.

A plot of $\ln r$ vs $\ln [C_6H_5NO_2]_{out}$ would give a straight line with slope m and intercept $\ln k'$. As shown in Fig. 3, the value of m , 0.67 ± 0.12 (the error range denotes 95% confidence limit), indicated a positive rate dependency on nitrobenzene at 440°C. Since the reaction order with nitrobenzene was determined to be 0.67 at 440°C, the following equation held:

$$\ln r - 0.67 \ln [C_6H_5NO_2]_{out} = n \ln [H_2O] + \ln k$$

It is indicated in Fig. 4 that the reaction order with supercritical water was statistically zero (-0.40 ± 0.72) at 440°C. The observed dependencies of the decomposition rate on nitrobenzene and supercritical water were taken into consideration for the design of the subsequent kinetic experiments.

More extensive experiments were conducted to determine the kinetic parameters over the temperature range from 440 to 550°C. The values of the kinetic parameters were

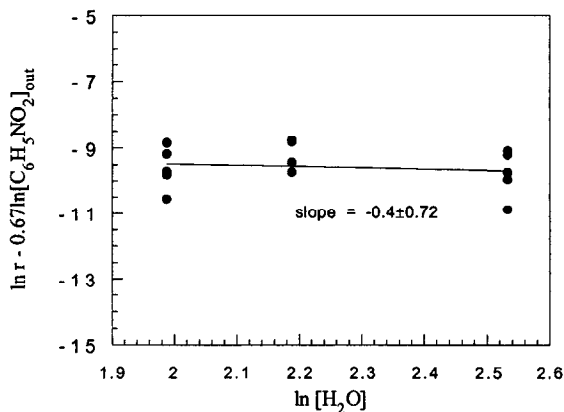


Fig. 4. Determination of reaction order with SCW at 440°C.

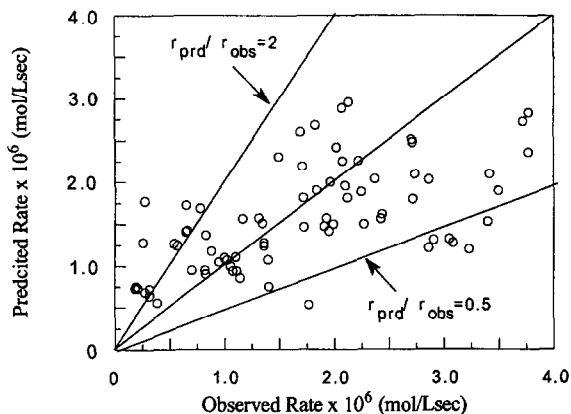


Fig. 5. Comparison of predicted and observed decomposition rates of nitrobenzene in SCW.

estimated by using SAS nonlinear regression analysis. The empirical power-law rate equation over this temperature range was determined as follows:

$$r = (1.2 \pm 4.9) \exp\left(\frac{-68.0 \pm 9.0}{RT}\right) [\text{C}_6\text{H}_5\text{NO}_2]^{0.39 \pm 0.18} [\text{H}_2\text{O}]^{0.21 \pm 0.48}$$

where R is the universal gas constant in $\text{kJ}(\text{molK})^{-1}$ and the errors are at 95% confidence limit. It follows from this result that the decomposition rate appeared to have a weak dependency on nitrobenzene while the density of supercritical water had no apparent effect under the experimental conditions. As shown in Fig. 5, the majority of the rates predicted by this rate equation was such that $r_{\text{predicted}}/r_{\text{observed}}$ fell within the range from 0.5 to 2.0.

3.2. Product analyses

Benzene was the only decomposition product identified in the liquid phase effluents. A typical trend of benzene formation with retention time is shown in Fig. 6. As

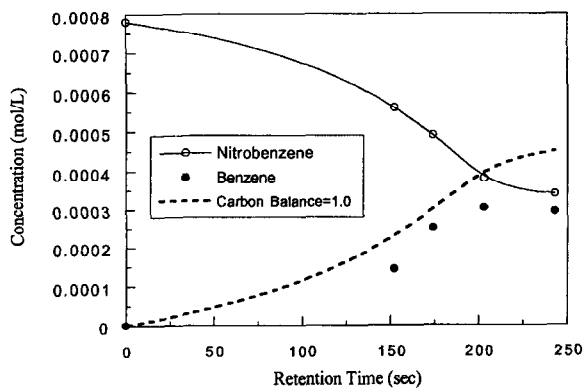


Fig. 6. Formation of benzene as a nitrobenzene decomposition product in SCW at 500°C.

nitrobenzene decomposed, the benzene concentration increased. Benzene in the liquid phase effluent accounted for about 85% of the carbon of the decomposed nitrobenzene. However, the benzene concentration started to decrease as the retention time extended. The decrease in the benzene concentration was more pronounced at higher temperature, which implies that benzene also underwent decomposition in SCW. Taking the benzene loss due to the benzene decomposition and to volatilization into gas phase effluents (which was detected but not quantified) into consideration, benzene was likely to be the only stable organic product of nitrobenzene decomposition. In the gas phase effluents, carbon monoxide, carbon dioxide and benzene were found. This indicated that the decomposition of nitrobenzene primarily underwent C–N bond breaking to form benzene which, for further decomposition, required extended retention time or high temperature. Once the benzene ring ruptured, however, the reaction proceeded to the mineralization as evidenced by the presence of carbon monoxide and carbon dioxide in the gas phase effluent. The primary source of oxygen for the mineralization was thought to be supercritical water [18]. While such an oxidative role of supercritical water might be still operative in the present experimental conditions, the possibility of oxidation by the nitro-group should also be noted. As shown in Figs. 7 and 8, respectively, the primary nitrogen species in the aqueous phase effluent was nitrite (NO_2^-) and the limited change in the density of supercritical water did not affect the nitrite yield. The yield of nitrite, however, decreased from about 0.5 to 0.1 with retention time. As shown in Fig. 9, the decrease in the nitrite yield corresponded to the increase in N_2 concentration in the gas phase effluent, which strongly suggested that the nitro-N underwent reduction to form N_2 . The reduction might drive the oxidation of organic carbon to produce carbon monoxide and carbon dioxide. Minor fractions of nitrogen of the decomposed nitrobenzene were converted to ammonia and nitrate (NO_3^-). Although the yields of such species were limited to less than 10%, it is interesting to note that both oxidized and reduced nitrogen species were simultaneously found. Fig. 10 indicates that the yield of ammonia and nitrate did not change with the supercritical water density in the present experimental conditions.

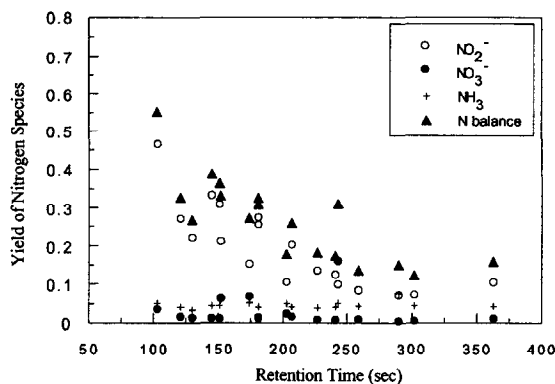


Fig. 7. Nitrogen speciation (as observed in aqueous phase effluent) after nitrobenzene decomposition in SCW at 500°C.

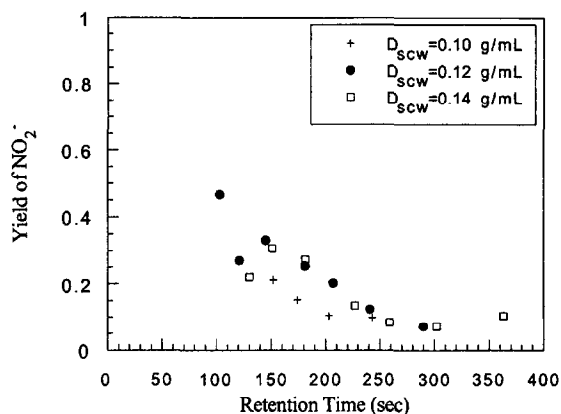


Fig. 8. Effect of SCW density on NO₂⁻ yield as observed in aqueous phase effluent.

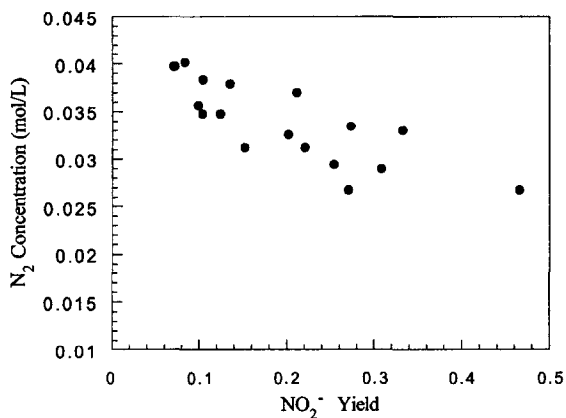


Fig. 9. Correlation of N₂ and NO₂⁻ yield as observed in effluent ($T = 500^{\circ}\text{C}$).

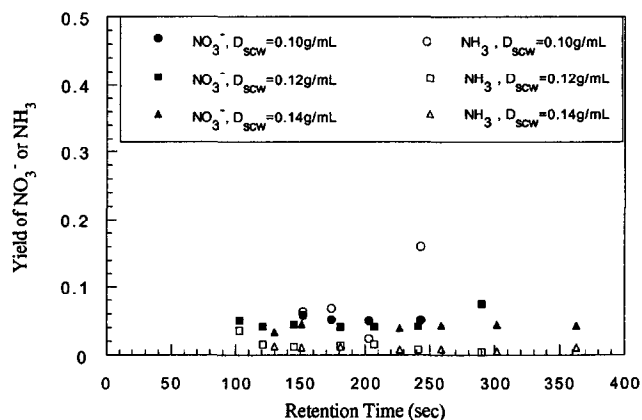


Fig. 10. Effect of SCW density on NO₃⁻ and NH₃ yields as observed in aqueous phase effluent.

3.3. Decomposition in the presence of oxygen

To investigate the effect of oxygen on the decomposition of nitrobenzene, the batch oxidation tests were conducted at 440°C. The decomposition kinetics of nitrobenzene were substantially enhanced in the presence of oxygen as shown in Fig. 11. The products analysis on the liquid phase effluent indicated that aniline, phenol, 2-(2-pyridinyl)-benzotrile, and dibenzofuran formed as end products. Such results suggested that the oxidation was the dominant destruction pathway and the presence of oxygen incurred complex reactions as compared to those in the oxygen absent system. The benzene ring existed in all end products, which was indicative of the stability of the benzene ring in SCWO conditions. The formation of dibenzofuran was reported in a previous study [22]. Dibenzofuran is of particular interest in that the possibility to form chlorinated dibenzofurans, if chlorine is present, should be noted. As is well known, chlorinated dibenzofurans and dibenzo-*p*-dioxins, are much concerned compounds for their toxicity. As compared to incineration, SCWO has been claimed to possess intrinsically higher potential of complete oxidation [4]. The result in the present study indicated that such potential might be realized only when careful selections of the appropriate reaction conditions are made.

In the presence of oxygen, the sum of the yields of ammonia, nitrite and nitrate was less than 10%. When the reaction temperature (440°C) is too low to form NO_x , the balance nitrogen is expected to take the form of nitrogen gas (N_2) under SCWO conditions [19]. Since the intrusion of air into the sampling bags during the gas sampling procedure could not completely be avoided in the present batch tests, the formation of nitrogen gas was confirmed only in a qualitative sense by examining the peak area ratio of nitrogen gas to oxygen gas. The ratio was about four with air, hence, if no nitrogen gas formed during the reaction, the ratio of the gas effluent would be smaller than four because of the excess oxygen present in the reactor. The observed ratio for the gas effluents was larger than four, typically ranging from six to 10. Therefore, it was concluded that nitrogen gas also formed in the presence of oxygen.

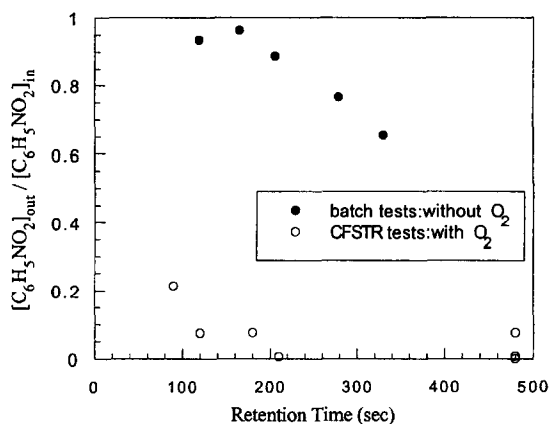


Fig. 11. Enhanced nitrobenzene destruction in the presence of oxygen at $T = 440^\circ\text{C}$, $D_{\text{scw}} = 0.25 \text{ g ml}^{-1}$.

4. Summary and conclusions

In the absence of oxygen, nitrobenzene decomposed in SCW to form primarily benzene and nitrite. The decomposition kinetics had an activation energy of $68.0 \pm 9.0 \text{ kJ mol}^{-1}$. Nitrobenzene concentration showed a weak effect on the decomposition kinetics whereas the density of SCW had no effect. Additional decomposition products such as carbon monoxide and carbon dioxide suggested the occurrence of oxidation driven possibly by SCW and nitro-group. The oxidative role of nitro-group was supported by the observation of the reduction of nitrite to N_2 gas.

The decomposition rate was substantially enhanced in the presence of oxygen. The oxidation yielded a number of aromatic reaction products including aniline, phenol, 2-(2-pyridinyl)-benzotrile, and dibenzofuran. The nitrogen in the decomposed nitrobenzene appeared to form mainly nitrogen gas even in the oxidative environments.

Acknowledgements

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References

- [1] S.H. Timberlake, G.T. Hong, M. Simson and M. Modell, *SAE Technol. Paper Ser. no. 820872* (1982).
- [2] M. Modell, G.C. Gaudet, M. Simson, G.T. Hong and K. Bieman, *Solid Wastes Mgmt*, August (1982).
- [3] C.M. Price, *S. M. Thesis*, Massachusetts Institute of Technology, MA, 1981.
- [4] M. Modell, in *Detoxification and Disposal of Hazardous Organic Chemicals By Processing in Supercritical Water*, Final Report, Department of Army Contract Number DAMD 17-80-C-0078, Natick, MA, 1987.
- [5] R.K. Helling, *Sc.D. Dissertation*, Massachusetts Institute of Technology, MA, 1986.
- [6] R.K. Helling and J.W. Tester, *Energy Fuel*, 1 (1987) 417.
- [7] H.H. Yang and C.A. Eckert, *Ind. Engng Chem. Res.*, 27 (1988) 2009.
- [8] C.K. Rofer and G.E. Streit, in *Kinetics and Mechanism of Methane Oxidation in Supercritical Water*, Report Number LA-11439-MS, DOE/HWP-64, Los Alamos National Laboratory, NM, 1988.
- [9] R. Li, T.D. Thornton and P.E. Savage, *Envir. Sci. Technol.*, 26 (1992) 2388.
- [10] P.A. Webley, J.W. Tester and H.R. Holgate, *Ind. Engng Chem. Res.*, 30 (1991) 1745.
- [11] D.S. Lee and E.F. Gloyna, *Envir. Sci. Technol.*, 26 (1992) 1587.
- [12] R. Li, T.D. Thornton, and D. Szumuckler, *AIChE. J.*, 39 (1993) 178.
- [13] T.T. Lira and P.J. McCrackin, *Ind. Engng Chem. Res.*, 32 (1993) 2608.
- [14] D.S. Lee, A. Kanthasamy and E.F. Gloyna, presented at *AIChE Annual Meeting*, Los Angeles, CA, 17–22 November, 1991.
- [15] S. Townsend, M. Abraham, G. Huppert, M. Klein and S. Paspek, *Ind. Engng Chem. Res.* 27 (1988) 143.
- [16] T.J. Houser, Y. Zhou, C.C. Chao and X. Liu, presented at *AIChE Annual Meeting*, Los Angeles, CA, 17–22 November, 1991.
- [17] D.M. Tiffany, T.J. Houser, M.E. McCarville and M.E. Houghton, *Am. Chem. Soc., Div. Fuel. Chem.*, 29 (1984) 56.
- [18] T.J. Houser, D.M. Tiffany, Z. Li, M.E. McCarville and M.E. Houghton, *Fuel*, 65 (1986) 827.
- [19] W.R. Killea, K.C. Swallow and G.T. Hong, *J. Supercritical Fluids*, 5 (1992) 72.
- [20] N. Crain, S. Tebbal, L. Li and E.F. Gloyna, *Ind. Engng Chem. Res.*, 32 (1993) 2559.
- [21] L. Li, E.F. Gloyna and J.E. Sawicki, *Water Envir. Res.*, 65 (1993) 250.
- [22] T.D. Thornton, D.E. LaDue and P.E. Savage, *Envir. Sci. Technol.*, 25 (1991) 1507.