

SUPERCRITICAL WATER OXIDATION OF UREA

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Abstract

Urea in an aqueous solution was decomposed under sub- and supercritical conditions of water in the presence and the absence of hydrogen peroxide at temperatures from 553 to 693 K at 23 MPa in a continuous flow reactor. The major products with and without H₂O₂ were carbon dioxide and ammonia. A small amount of OCN⁻ was also detected without H₂O₂, and NO₃⁻ and NO₂⁻ were produced with H₂O₂. The decomposition reactions of urea with and without H₂O₂ were represented by the first order reaction kinetics, and the pre-exponential factors and the activation energies were 17 s⁻¹ and 73 kJ mol⁻¹ with H₂O₂, and 20 s⁻¹ and 93 kJ mol⁻¹ without H₂O₂, respectively, at temperatures from 573 to 643 K. The presence of NaCl did not affect the product distribution significantly, but enhanced the rates at temperatures higher than 653 K.

Introduction

Supercritical water oxidation has been extensively studied for the decomposition of various organic compounds due to extremely fast reaction rates and substantially complete decomposition into carbon dioxide and water. However, in case of organic compounds containing nitrogen atoms, ammonia is produced and it is one of the most refractory products. Many efforts have been made to study supercritical water oxidation of nitrogen containing compounds such as amide [1,2], ammonia [3-6], aniline [7], nitrate [8,9], nitrile [10,12], pyridine [13], waste water [14,15] etc.

Urea is contained in wastewater sources such as human waste, effluent from manure pit in farm land etc. Although a biological treatment is effective, an alternative disposal method is also required because Japanese land is highly populated and mountainous. Since the supercritical water oxidation is capable of achieving fast reaction rate and nearly complete conversion, it is one of candidates for the disposal method of wastewater containing urea. However, the oxidative decomposition of urea has not been well studied under sub- and supercritical conditions. In this study urea in an aqueous solution was subjected to sub- and supercritical water with/without hydrogen peroxide. The major products were measured and the decomposition rates were determined in a continuous flow reactor. In the presence of NaCl, which often is contained in real wastewater, the effects of the presence of NaCl on the product distribution and the rates were also studied.

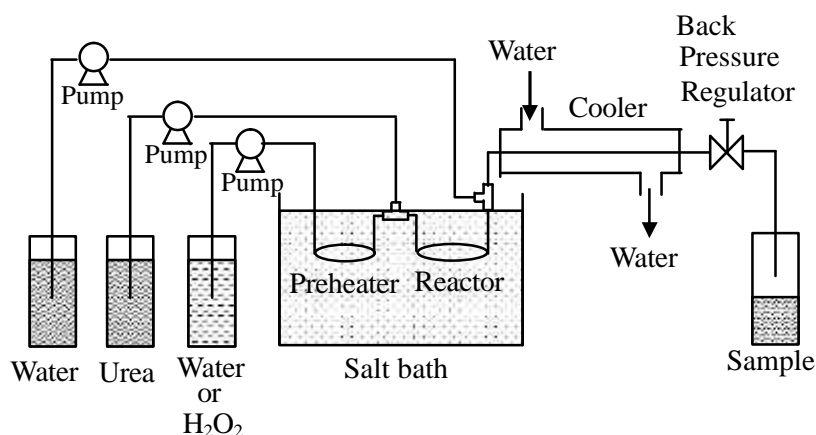


Fig. 1 A schematic diagram of experimental apparatus

Experimental apparatus and procedures

A schematic diagram of the experimental apparatus is shown in Figure 1. The three tubings in different lengths of 80, 150, and 300 mm, made of stainless steel tubings with 0.25 mm I.D., were employed as a reactor. An aqueous solution of urea was supplied by a HPLC pump, and hydrogen peroxide aqueous solution by a syringe pump. The urea concentrations were varied from 0.1 to 1 mol L⁻¹. Water or H₂O₂ aqueous solution was continuously supplied by a syringe pump to a preheater column, made of 0.25 mm inner diameter of stainless steel tubing (1000 mm long), which was immersed in a molten salt bath, equipped with a stirrer, whose temperature was maintained at a prescribed temperature within the fluctuation of ± 2 K. Water with/without H₂O₂ heated in the preheater column and the urea solution supplied by a HPLC pump were mixed at a T-junction, placed just upstream at the reactor inlet. Cold distilled water was also supplied by a HPLC pump, and just merged to the reacted solution at a T-junction, placed at the reactor exit to cool down the solution. The solution was further quenched by a water jacket in which cold water was flowing. The reactor pressure was maintained at 23 MPa by a back pressure regulator, placed at the end of the line, which was capable of controlling the pressure within ± 0.1 MPa by a high frequency open-shut valve operated electro-magnetically. The flow rates of the urea, hydrogen peroxide and quenching water were set to be equal for each run. The residence time of the solution was estimated by

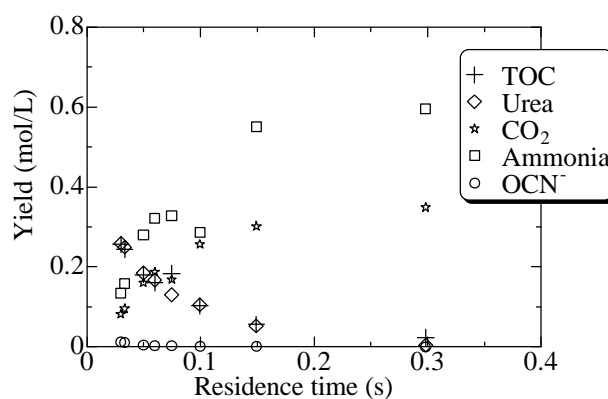


Figure 2 Yields vs. residence time at 633K without H₂O₂

residence time of the solution was estimated by

the flow rates, assuming it as a plug flow. The density was estimated by the equation of state proposed by Saul and Wagner [16], assuming that the densities of the solutions were equal to those of pure water because of low concentrations. The product solution eluted from the exit of the back pressure regulator was collected at every one to three minutes. Contents of total organic carbon, inorganic carbon and total nitrogen were measured by a TC/TN analyzer. The amount of urea remained in the solution was measured by a HPLC. The ionic nitrogen compounds were measured by an ion chromatograph and a capillary electrophoresis apparatus. The ammonia yield was also measured by a GC.

Results and Discussion

Figure 2 shows product yields vs. residence time at 633 K in the absence of hydrogen peroxide. By changing the flow rates and/or replacing with the different length of the reactor, the residence time was varied. The amount of urea remained and the TOC content simply decreased with increasing the residence time. The organic carbon detected was found to be only come from urea remained because TOC content was fully consistent with the amount of urea remained. No other organic compound was found to be produced. Yields of carbon dioxide and ammonia increased with the residence time similarly, but the ammonia yields were roughly twice as much as those of carbon dioxide. At the residence times longer than 0.15 s both yields became nearly saturated. Production of OCN^- was observed, but the yields were low.

Figure 3 shows OCN^- yield vs. residence time at various temperatures without hydrogen peroxide. The maximum yields of OCN^- were observed to be as high as 5 mol% of initial urea at short residence

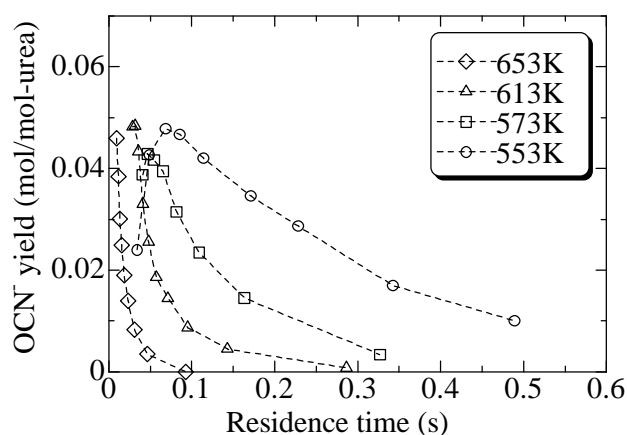


Figure 3 OCN^- yields vs. residence time without H_2O_2

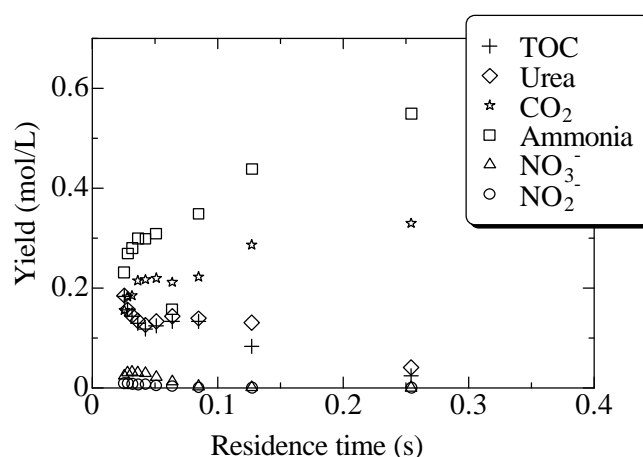


Figure 4 Yields vs. residence time at 633K with 5wt% H_2O_2 aq.

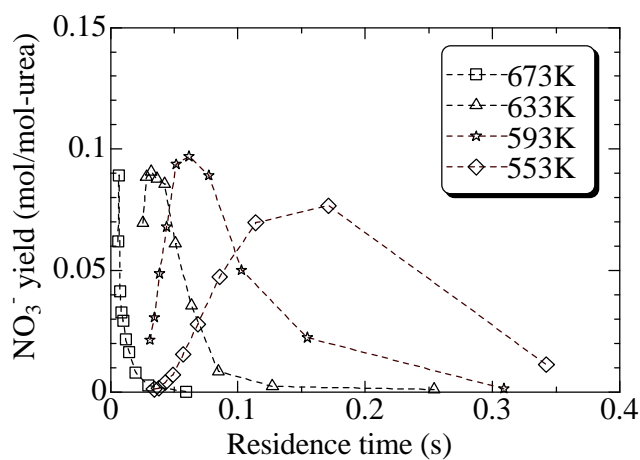


Figure 5 NO_3^- yields vs. residence time with 5wt% H_2O_2 aq.

times and all temperatures. The yields at lower temperatures were higher, and the yields at all temperatures decreased with increasing residence time. At 653 K the yield became nearly zero within 0.1 s. Figure 4 shows product yields vs. residence time at 633 K with 5wt% hydrogen peroxide. Both contents of TOC and the amount of urea remained decreased with increasing residence time, similarly to those without H_2O_2 as shown in Figure 2. However, the CNO^- yields were much lower than those without H_2O_2 .

Figures 5 and 6 plot yields of nitric ion NO_3^- and nitrous ion NO_2^- , respectively, against residence time at temperatures from 553 to 673 K. The NO_3^- yields at shorter residence times were nearly zero, and increased with times at higher temperatures. The yields reached the maxima and decreased thereafter. The yields at the highest temperature of 673 K decreased with time because the times showing the maximum values seemed to be extremely short. The maximum yields were as high as 8 to 10 mol% of initial urea at all temperatures. The yields of NO_2^- showed similar behaviors to those for NO_3^- , but the yields were lower. The residence times showing the maximum yields were shorter than those for NO_3^- .

Figure 7 shows the effect of H_2O_2 concentration on time change of NO_3^- yield over the range of H_2O_2 concentrations from 2.5 to 10 wt%. At all concentrations, the yields increased with time, reached the maximum values, and then decreased gradually. The maximum values at higher concentrations were higher, and reached them at longer residence times.

Figure 8 shows product yields vs. residence time with NaCl concentration of 0.5 mol L^{-1} . Substantially the product distribution with NaCl was similar to that

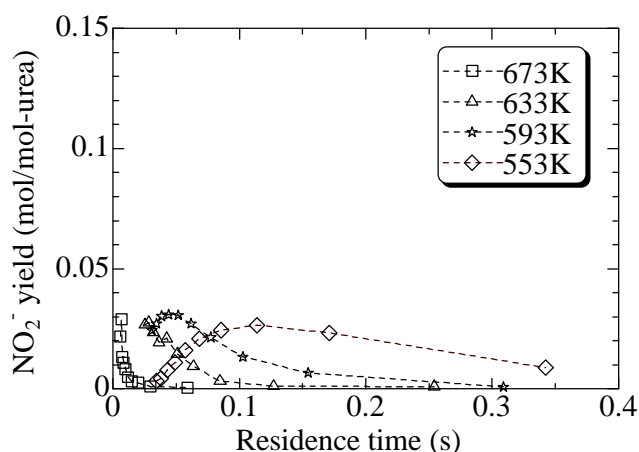


Figure 6 NO_2^- yields vs. residence time with 5 wt% H_2O_2 aq.

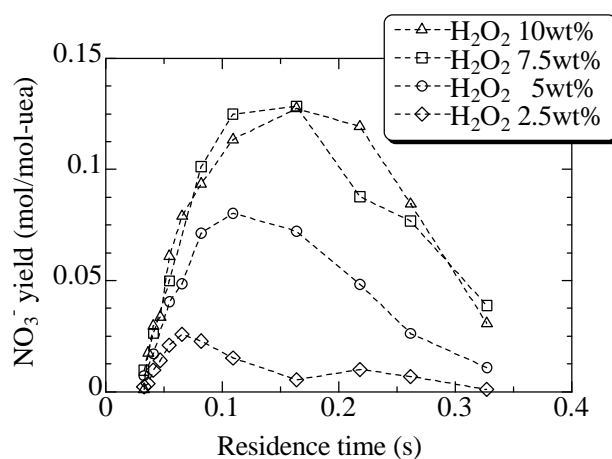


Figure 7 NO_3^- yields vs. residence time at 573K for 1mol/L-urea

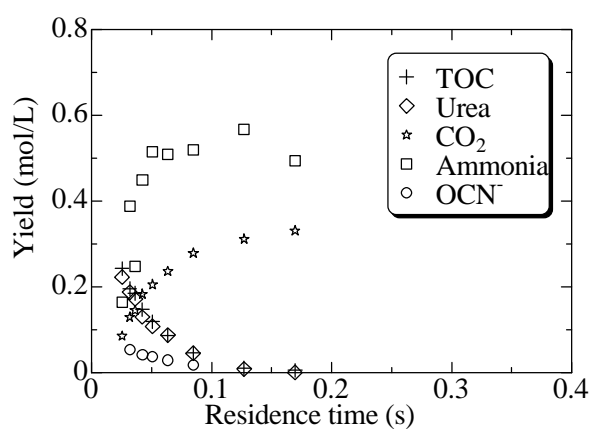


Figure 8 Yields vs. residence time at 633K with 0.5 mol/L-NaCl

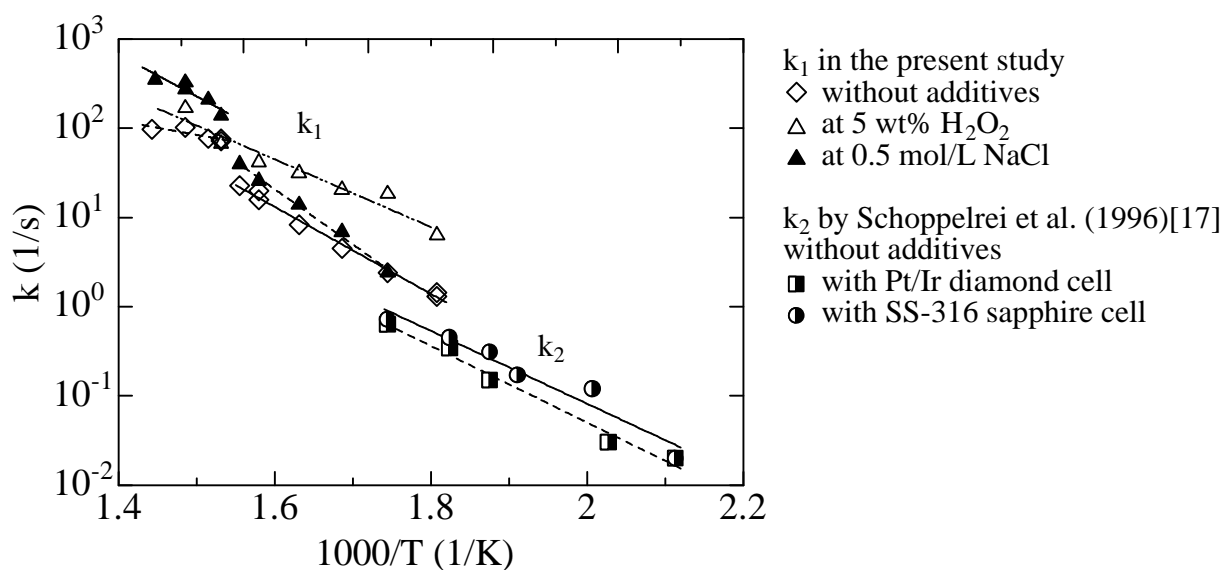
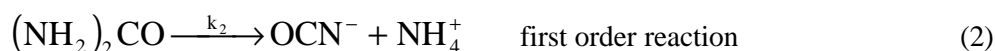


Figure 9 Arrhenius plots of reaction rate constants for the decomposition of urea



without. However, the OCN^- yields increased somewhat as compared with those without NaCl.

Figure 9 shows Arrhenius plots of rate constants of the urea decomposition reaction, assuming that the reaction can be represented by the first order reaction kinetics with respect to urea concentration in eq (1), together with the rates of eq (2) obtained by Schoppelrei et al. [17]. Note that k_1 , k_2 and k_3 denote rate constants of eqs (1), (2) and (3), respectively. Schoppelrei et al. [17] carried out the reaction in two optical cells, made of Pt/Ir with diamond windows and SUS-316 stainless steel with sapphire windows, by monitoring the product yields continuously with an FTIR spectrometer. They determined the rates based on two consecutive reaction paths in eqs (2) and (3), and found that the values were affected by the cell material. In the present study without the oxidant, the pre-exponential factor and the activation energy for k_1 were obtained to be 20 s^{-1} and 93 kJ mol^{-1} at temperatures from 573 to 643 K, respectively. When hydrogen peroxide concentration was 5 wt%, they were 17 s^{-1} and 73 kJ mol^{-1} in the same temperature range. Although the effect of NaCl added on the decomposition rates was not observed below 653 K, the presence of NaCl enhanced the rates above 653K.

Conclusions

Urea in an aqueous solution was decomposed under sub- and supercritical conditions of water in the presence and the absence of hydrogen peroxide in a continuous flow tubular reactor. The major products with/without H_2O_2 were similar, except for NO_3^- and NO_2^- with

H₂O₂. The major products were ammonia and carbon dioxide. The yields of ammonia were almost twice as much as those of carbon dioxide on mole fraction basis. OCN⁻ was observed as an intermediate in the absence of hydrogen peroxide. In the presence of H₂O₂, NO₃⁻ and NO₂⁻ were detected, and the OCN⁻ yields were much lower than those without H₂O₂. The presence of NaCl did not drastically affect the product distribution, but the rate was slightly increased above 653 K.

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