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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Decomposition of urea in sub- and supercritical water with/without additives

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Abstract Urea was decomposed in sub- and supercritical water in the presence and the absence of hydrogen peroxide at temperatures from 538 to 651 K, 23 MPa and residence times up to 1.5 s in a continuous flow reactor. The initial concentrations of urea varied from 0.005 to 0.5 mol L^{-1}. The major products were carbon dioxide, and ammonia. As a minor product cyanic acid was detected without hydrogen peroxide, and nitric acid and nitrous acid were produced with hydrogen peroxide. The decomposition rates of urea with and without hydrogen peroxide were represented by the first order reaction kinetics. The addition of hydrogen peroxide increased the rates at lower temperatures, but was scarcely effective at higher temperatures. In the absence of hydrogen peroxide, the effects of various additives at concentrations of 0.5 mol L^{-1} on the decomposition rates at 649 K were examined. The addition of NaOH enhanced them remarkably. The presence of NaCl did not affect the product distribution significantly, but enhanced the rates somewhat, in particular, increasing as approaching to the critical temperature of water. The addition of acids, hydrogen chloride and sulfuric acid, did not increase the rates.

Introduction

Sub- and supercritical water has been considered to be an attractive solvent because it works as not only a solvent but also a reactant to decompose organic pollutants contained in wastewaters in chemical, food, agricultural, poultry, fishery industries as well as in municipal human wastewater etc. Supercritical water oxidation (SCWO) 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 [1, 2]. However, in case of organic compounds containing nitrogen atoms, ammonia, one of the most refractory products, is produced. Many efforts have been made to study supercritical water oxidation of nitrogen containing compounds such as amid [3–5], ammonia [6–8], aniline [9], nitrate [10], nitrile [11–13], pyridine [14], wastewater [15–17] etc. Although such wastewaters often contain NaCl, the effects of the salt on the decomposition rates and the product distribution have not been well studied in SCWO of nitrogen containing compounds.

Urea is contained in wastewater sources such as human waste and a breakdown product of animal proteins, effluent from manure pit in livestock farm yard, decomposition product of urethane, etc. Although a biological treatment for urea is effective, an alternative disposal method is also required because the biological treatment needs long time. Since SCWO is capable of achieving fast reaction rate and nearly complete conversion, it is one of candidates for the disposal method of the wastewaters.

While the previous studies focus mainly on decomposition of urea in water at 373 K and atmospheric pressure [18–23], the studies under high pressures are limited: Kieke et al. [24] and Schoppelrei et al. [25] proposed the reaction pathways and determined the decomposition rates by infrared spectroscopy measurements in urea decomposition at temperatures from 473 to 573 K and 27.5 MPa. Moreover, the effect of additives on urea decomposition in sub- and supercritical water has not been examined.

In this study urea was subjected to sub- and supercritical water with/without hydrogen peroxide. The major products

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were measured and the decomposition rates were determined in a continuous flow reactor. Moreover, the effects of various additives on the product distribution and the rates were also studied.

Experimental apparatus and procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reaction was carried out isothermally at temperatures from 538 to 651 K and a constant pressure of 23 MPa. The 300 and 600 mm tubes, made of stainless steel tubings with 0.25 mm I.D., were employed as a reactor. Aqueous solutions of urea (purity of 99% obtained from Kanto Chem. Co., Tokyo, Japan) at various concentrations from 0.01 to 1 mol L^{-1} were degassed sufficiently by ultrasonic wave, and then supplied to the reactor by a HPLC pump (Model L-6000, Hitachi, Japan). An another solution (water or various additive solutions) fed by a syringe pump (Model 100DM, ISCO, U.S.A.) was heated in a preheating column, made of 0.25 mm inner diameter of stainless-steel tubing in 1000 mm long, which was immersed in a stirrer equipped molten salt bath, whose temperature was maintained at a prescribed temperature within the fluctuation ±1 K. The heated aqueous solution was mixed with the urea solution fed separately on the same axis but in the opposite direction in the T-union. Cold distilled water was also supplied by a HPLC pump, and just merged to the product solution eluted from the reactor in a T-union, placed at the exit of the reactor to terminate the reaction. The mixed solution was further quenched by a water jacket in which cold water was flowing. To obtain various residence times of the solutions, the flow rates were changed such that the flow rates of the urea solution, the aqueous solution and the quenching water were the same value for each run. Note that the concentrations of urea and the additives described in the text and figures are those at the reactor inlet unless specified.

Measurements of fluid temperatures were made apart from reaction experiments. Figure 2 shows details of the reactor used for fluid temperature measurements. Temperatures of the fluid at different distances from the inlet, by replacing a tubing having different length (40, 80, 150, 220, and 300 mm), were directly measured with a thermocouple placed in a T-union at the exit. As a result, certain heating periods were found to be required to reach the prescribed temperatures, e.g. 0.12 s for the prescribed temperature of 651 K. The residence time of the solution was estimated by the flow rate, the reactor volume, and the fluid density, assuming that the properties of the solution were the same as pure water due to the dilute solution, and it moved in a plug flow. The density was obtained by the equation of state proposed by Saul and Wagner [26]. The reaction pressure was maintained at 23 MPa by a back pressure regulator, placed at the end of the line, which is capable of controlling the pressure within ±0.1 MPa by a high frequency open-shut valve operated electro-magnetically. After the system had reached the steady state conditions, the solution eluted from the exit of the back pressure regulator was collected periodically, and analyzed. Total organic carbon (TOC) and total nitrogen (TN) contents were measured by a TC and TN analyzer (TOC-V, Shimadzu, Japan). The amount of urea remained in the solution was measured by a HPLC. The ionic nitrogen compounds were measured by an ion chromatograph (DX-120, Dionex, USA) and a capillary electrophoresis apparatus (CAPI-3300, Otsuka Electronics Co., Japan). The ammonia yield was also measured by a GC.

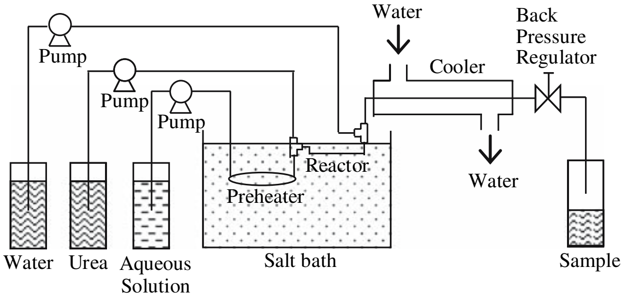


Fig. 1 A schematic diagram of the experimental set-up

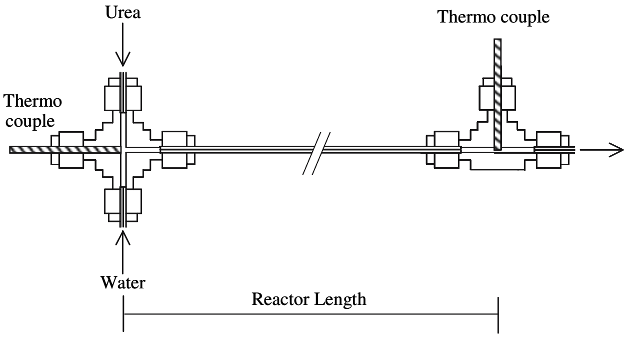


Fig. 2 Details of the reactor assembly to measure fluid temperature

Results and discussion

Product distribution

Without hydrogen peroxide

Figure 3 shows time changes of product yields and TOC value, together with the quantity of urea remained at 558 K in the absence and the presence of hydrogen peroxide. In the presence of hydrogen peroxide the results are described in next section. The major products were ammonia and carbon dioxide. The amount of urea remained and the TOC content simply decreased with increasing residence time. The TOC detected was found to be mainly ascribed to urea remained because TOC content was almost consistent with the amount of urea remained on carbon weight basis. Yields of carbon dioxide and ammonia increased with residence time similarly, but the ammonia yields were roughly twice as much as those of carbon dioxide. Production of OCN^- was observed, but the yields were low.

Figure 4 shows OCN^- yield vs. residence time at various temperatures without additives. The maximum yields of OCN^- were observed to be as high as 5 mol% of the initial urea at short residence times and all temperatures. The yields at lower temperatures were higher, and the yields at all temperatures decreased with increasing residence time. At 636 K the yield became nearly zero within 0.5 s.

Figure 5 shows the effect of initial urea concentration on time change of OCN^- yield over a range of urea concentration from 0.005 to 0.5 mol L^{-1} at 558 K. At all concentrations, the maximum yields at lower initial concentration were higher, and times showing the maximum values were longer.

With hydrogen peroxide

The effects of the addition of hydrogen peroxide on the product yields and the quantities of TOC and urea remained at 558 K are shown in Fig. 3, as compared with those without oxidant. The major products were ammonia and carbon dioxide with/without oxidant, while nitric ion NO_3^- and nitrous ion NO_2^- were observed with hydrogen peroxide. The OCN^- yields were much lower than those without oxidant. Note that the residence times of the fluid were estimated by taking into account the volume change due to oxygen formed from hydrogen peroxide, which was completely decomposed into oxygen and water, as pointed out by Oshima et al. [27]. When the volume change is not considered, the residence times increase roughly up to 10%.

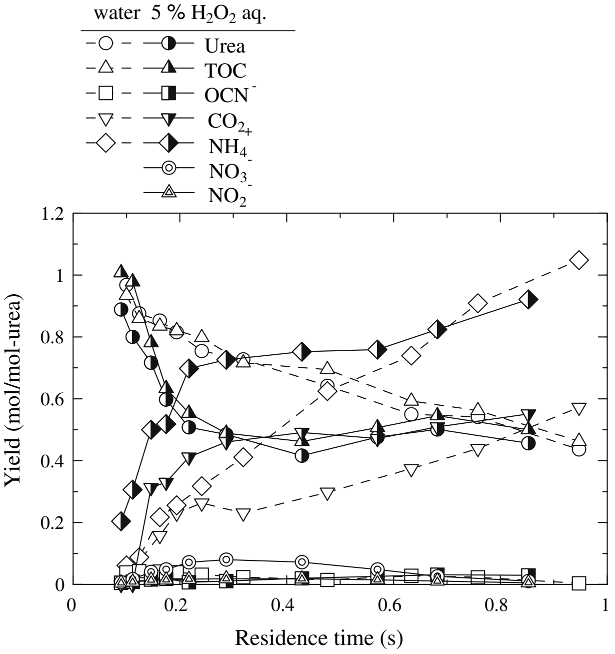


Fig. 3 Yields of various products and the amount of urea remained vs. residence time with and without hydrogen peroxide (5 wt%) at 558 K and initial urea concentration of 0.5 mol L^{-1}

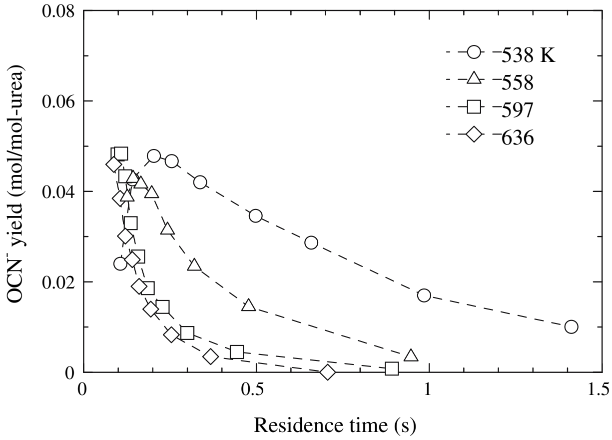


Fig. 4 OCN^{-1} yield vs. residence time at various temperatures without hydrogen peroxide

Figures 6 and 7 plot yields of NO_3^- and NO_2^-, respectively, against residence time at temperatures from 538 to 649 K. The NO_3^- yields at shorter residence times were nearly zero, and increased with times at higher temperatures. The NO_3^- yields reached the maximum values and decreased thereafter. The yield at the highest temperature

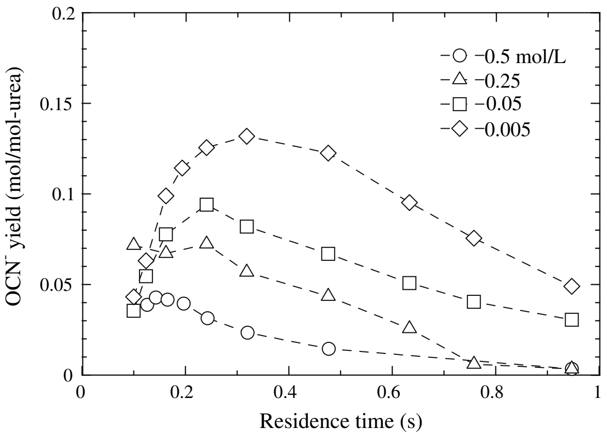


Fig. 5 OCN^{-1} yield vs. residence time at various initial urea concentrations at 558 K without hydrogen peroxide

of 649 K decreased with time because the time showing the maximum value 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 behavior to that for NO_3^-, but the yields were lower. The residence times showing the maximum yields were shorter than those for NO_3^-.

Figure 8 shows the effect of hydrogen peroxide concentration on time change of NO_3^- yield over a range of H_2O_2 concentration 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.

Decomposition rates

Since carbon dioxide and ammonia were produced in the molar ratio of 1 to 2 with and without hydrogen peroxide, the overall reaction pathway could be described in Eq. 1:

$$(NH_2)_2CO + H_2O \xrightarrow{k_1} CO_2 + 2NH_3 \tag{1}$$

When it can be assumed that the fluid moved in a plug flow and the overall urea decomposition reaction to be the first order reaction kinetics, the rate constant k_1 can be obtained from Eq. 2:

$$\ln\left(\frac{C}{C_1}\right) = -(t - t_1)k_1 \tag{2}$$

where C and C_1 are the urea concentrations at residence times t and t_1 ($t > t_1$), respectively, and t_1 was chosen at the shortest residence time at each temperature. The reaction rates were determined at residence times longer than t_1 because the urea decomposition in the heat-up zone in the vicinity of the reactor inlet was eliminated. Figure 9 shows Arrhenius plots for the rate constants k_1 so determined. In the present study without hydrogen peroxide the pre-exponential factor and the activation energy for k_1 were obtained to be 1.7×10^7 s^{-1} and 78 kJ mol^{-1}, respectively, at temperatures from 538 to 651 K and initial urea concentration of 0.5 mol L^{-1}. When hydrogen peroxide was added (5 wt% of aqueous solution), they were 2.1×10^5 s^{-1} and 51 kJ mol^{-1} at temperatures from 538 to 649 K. When the effect of water density on the overall rates are taken into account, in case of the hydrolysis reaction being dominant, the rate constants can be expressed as

$$k_1 = k_{10}[H_2O] \tag{3}$$

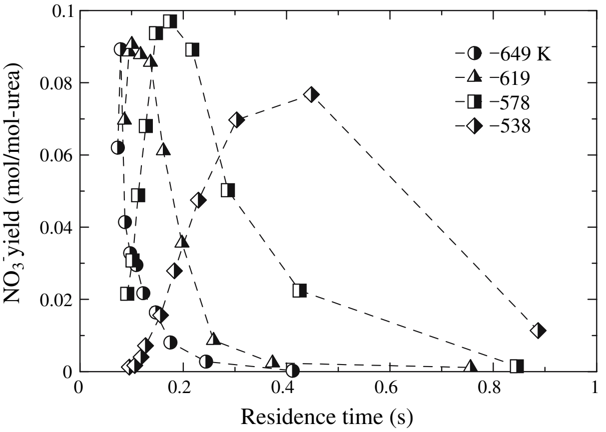


Fig. 6 NO_3^- yield vs. residence time at various temperatures and initial urea concentration of 0.5 mol L^{-1} with hydrogen peroxide (5 wt%)

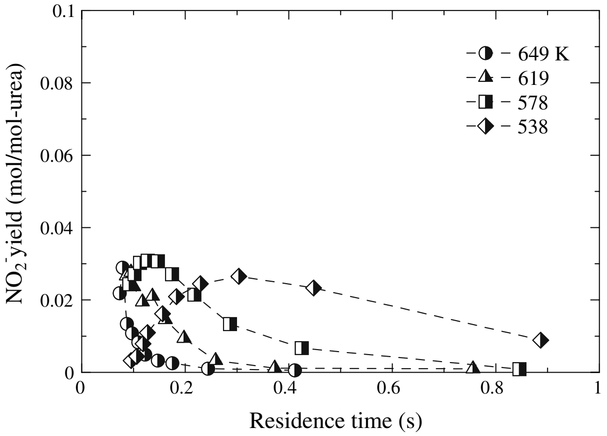


Fig. 7 NO_2^- yield vs. residence time at various temperatures and initial urea concentration of 0.5 mol L^{-1} with hydrogen peroxide (5 wt%)

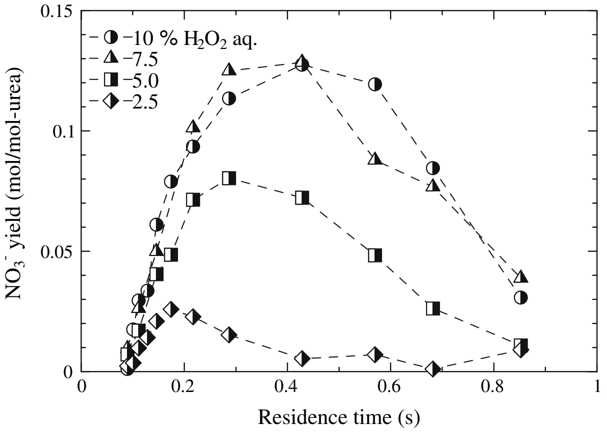


Fig. 8 NO_3^- yield vs. residence time at 558 K and initial urea concentration of 0.5 mol L^{-1} with hydrogen peroxide at various concentrations

where k_{10} is the rate constant and $[H_2O]$ is the water density. With/without hydrogen peroxide the values k_{10} were well represented, and the pre-exponential factor and the activation energy of k_{10} were 3.84×10^5 m^3 kg^{-1} s^{-1} and 91.4 kJ mol^{-1} with water, and 4.48×10^2 m^3 kg^{-1} s^{-1} and 52.2 kJ mol^{-1} with 5 wt% aqueous hydrogen peroxide solution, respectively.

The rate constants k_2 based on reaction models in Eqs. 4 and 5, proposed by Kieke et al. [24] and Schoppelrei et al. [25], were also plotted in Fig. 9.

$$(NH_2)_2CO \xrightarrow{k_2} OCN^- + NH_4^+ \quad \text{First order reaction} \tag{4}$$

$$OCN^- + NH_4^+(+H_2O) \xrightarrow{k_3} CO_2 + 2NH_3 \tag{5}$$
$$\text{Second order reaction}$$

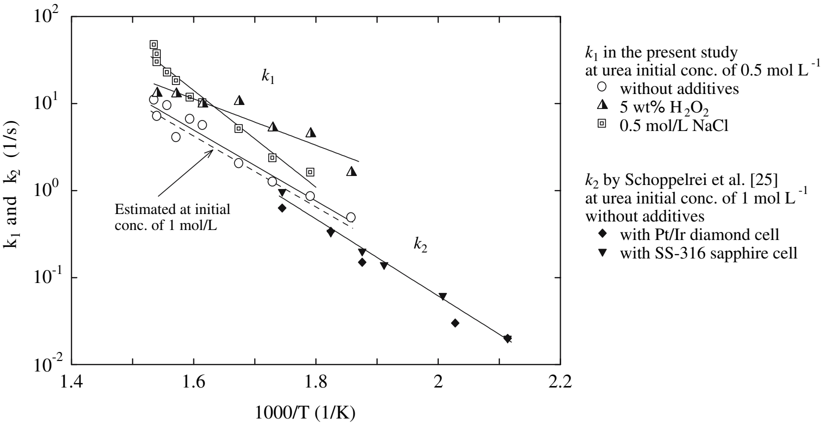
where k_2 and k_3 denote rate constants Eqs. 4 and 5, respectively. They [24, 25] carried out the reaction in an optical cell, made of Pt/Ir with diamond windows and SUS-316 stainless steel with sapphire windows, by monitoring the product yields continuously with an FTIR spectrometer. They determined the rates based on two consecutive reaction pathways in Eqs. 4 and 5. However, we assume that the reaction under the present conditions can be represented by Eq. 1 because the pathway in Eq. 5 is fast and the yields are low at high temperatures, as shown in Figs. 4 and 5. Figure 10 plots the effects of the initial urea concentration on the first order rate constants determined at 558 and 649 K. The rate constants at each temperature decreased with increasing the initial concentration having almost the same slopes, −2.5 and −2.1 at 558 K and 649 K, respectively. Since the initial urea concentration in the present study was 0.5 mol L^{-1}, the values of rate constrant k_1 were extrapolated from the correlation between the rate data and urea initial concentration, as shown in Fig. 10. As a result, the present values k_1 extrapolated at 1 mol L^{-1} (designated with a dashed line in Fig. 9) were nearly consistent with those extended from the k_2 values of Shoppelrei et al.

Effects of additives

Figure 11 shows the amount of urea remained C/C_0 vs. residence time in a semi-logarithmic plot for various additives such as NaCl, HCl, H_2SO_4 and NaOH, at 649 K, the initial urea concentration of 0.5 mol L^{-1} and the additive concentration of 0.05 mol L^{-1}, where C and C_0 were urea concentrations at residence time t and the initial value, respectively. Note that 649 K is considered to be lower than the critical temperatures of both solutions NaOH and NaCl at the concentrations of 0.05 mol L^{-1} [28]. The product distributions were not substantially affected by the additives of NaCl and H_2SO_4. NO_3^- and NO_2^- were not detected. All additives studied were effective for the decomposition of urea, in particular, NaOH enhanced the rates significantly. The reason is not clarified. However, it can be speculated that less quantity of ammonia may be dissociated under basic conditions, and the presence of ammonia may accelerate the decomposition of urea through nucleophilic reactions. It is interesting to note that urea kept being decomposed almost completely when the additives were present. Although urea without additives was decomposed with the almost same slope as those with additives, except for NaOH, in the major decomposition stage up to C/C_0 of 0.25, the reaction was suppressed at lower C/C_0 values without additives.

Figure 12 shows the effects of NaOH or NaCl concentration on the k_1 values. The rates increased slightly with increasing the concentration. The presence of NaCl at concentrations up to 0.5 mol L^{-1} scarcely affected the product distribution, but the rates were increased at all reaction temperatures studied. In particular, NaCl enhanced the rates at higher temperatures. When NaCl concentration

Fig. 9 Arrhenius plots for rate constants k_1 in the present study and k_2 in the literature [25]



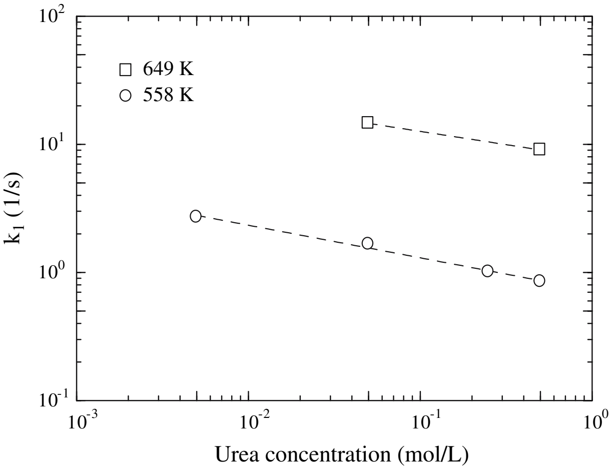


Fig. 10 Effect of initial urea concentration on rate constant for urea decomposition in Eq. 1 at two temperatures of 558 and 649 K without hydrogen peroxide

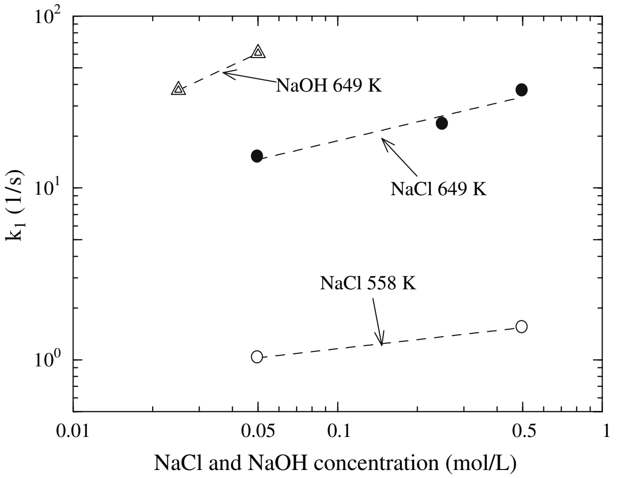


Fig. 12 Effect of NaCl or NaOH concentration on rate constant k_1 at initial urea concentration of 0.5 mol L^{-1}

was 0.5 mol L^{-1}, the pre-exponential factor and the activation energy were 1.1×10^{10} s^{-1} and 106 kJ mol^{-1} at temperatures from 558 to 651 K.

Conclusions

Urea was decomposed in sub- and supercritical 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 NH_3 and carbon dioxide, except for NO_3^- and NO_2^- with H_2O_2. 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 H_2O_2, NO_3^- and NO_2^- were detected, and the OCN^- yields were much lower than those without H_2O_2. The presence of NaCl at 0.5 mol L^{-1} did not drastically affect the product distribution, but the rate was increased in the temperature range from 558 K to 651 K. The urea decomposition rates, represented by the first order reaction kinetics, slightly showed the dependence of the initial urea concentration. The present decomposition rate constants k_1 extrapolated at 1 mol L^{-1} were nearly consistent with those extended from the literature values k_2 at low temperatures.

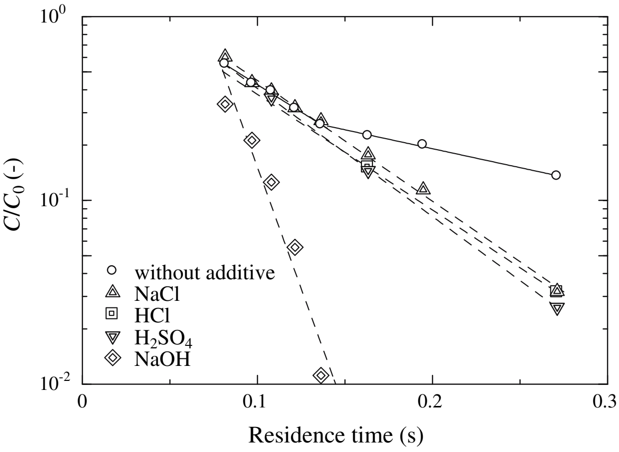


Fig. 11 Urea remained C/C_0 vs. residence time with various additives at 649 K, concentration of 0.05 mol L^{-1}, and initial urea concentration of 0.5 mol L^{-1}

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