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Effect of NaOH on the decomposition of halogenated hydrocarbon by supercritical water oxidation

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Abstract−To protect alloys from corrosion phenomena in the supercritical water oxidation (SCWO) process, the effects of neutralizer on the conversion and corrosion were investigated. The surface morphologies of all the alloy coupons exposed to 2,4-Dichlorophenol (2,4-DCP) in the SCWO were significantly changed in microscopic images. The theoretical amount of NaOH as a neutralizer was calculated under the assumption of complete oxidation of 2,4-DCP. The pre-dosed NaOH in the range of 100% to 300% stoichiometric amount could not affect significantly the pH value in the SCWO. Moreover, the pH=7 was not achieved until 700% stoichiometric amount of NaOH was pre-dosed to the reactor. It is noted that the conversion rate recorded over 99% without oxidant when 800% of NaOH was pre-dosed into the reactor. In addition, under the addition of H_2O_2 as an oxidant, the increased amount of NaOH led to the improvement of conversion rate. The pre-dosed NaOH may contribute to the conversion rate of 2,4-DCP in the SCWO. However, due to low solubility of salt in the SCWO, the fouling problem should be solved in the SCWO process.

Key words: Supercritical Water Oxidation, Corrosion, Neutralizer, Alloy, 2,4-DCP

INTRODUCTION

Since most organic compounds, as well as the oxidant and combustion gases, are miscible in all proportions with water in supercritical condition, the effective oxidation of organic materials and wastes can be possible in supercritical water (P>221 bar, T>374 °C) [Dell'Orco et al., 1997; Dinaro et al., 2000; Hatakeda et al., 1999; Goto et al., 1998; Martino and Savage, 1997; Zhou et al., 2000]. Therefore, in the last two decades, supercritical water oxidation (SCWO) has been actively developed as a means of destroying hazardous organic waste.

The properties of water, such as density, viscosity, diffusivity and static dielectric constant, are changed dramatically by a slightly different value of temperature and pressure at the near critical point. In addition, the static dielectric constant of supercritical water (SCW) is close to that of non-polar solvents because this value of SCW is so small (supercritical condition <2, atmospheric condition≈80) [Model, 1986; Konys et al., 1999]. And hydrogen bonding decreases with a decrease in water density. Therefore, since organic compounds and gases become completely miscible with the SCW, reaction can occur in single phase and mass transfer resistance becomes negligible [Connolly, 1966; Lee et al., 2005; Kang and Chun, 2004].

These properties of supercritical water enable toxic and refractory compounds to be destroyed with high decomposition efficiency and short reaction time. However, for the treatment of halogenated compounds, both corrosion problems by acid and fouling problems by low solubility of inorganic salts should be considered for its successful application [Peter and Eckhard, 2001; Kritzer et al., 1998]. Furthermore, the operational safety of the SCWO process should be considered first because corrosion phenomena might bring about serious hazards. Therefore, it is essential to figure out the role of neutralizer on the SCWO of halogenated hydrocarbons for effective as well as safe operation of the SCWO process.

In this study, the corrosion phenomena of various alloys in the SCWO process were measured by microscopic investigation. The materials chosen for corrosion test include Titanium Gr7, Inconel 601, Inconel 625, Inconel 825 and Nickel, which are known for the high corrosion-resistant materials under high acid condition. The corrosion test was performed at severe SCWO condition such as near critical temperature, relatively high concentration of Cl-compound and H_2O_2 conditions. In addition, the theoretical and experimental quantity of NaOH to neutralize the effluent in the SCWO of 2,4-DCP with oxidant H_2O_2 were investigated. The effects of pre-dosed NaOH on the pH and conversion rate in the SCWO were also studied.

EXPERIMENTAL PROCEDURE AND ANALYTICAL METHODS

In this study, 2,4-Dichlorophenol (2,4-DCP, $C_6H_4Cl_2O$, 99% purity, Acros Organics Co. Ltd.) was selected as a representative halogenated compound at SCWO. Once 2,4-DCP was dissolved in secondary purified water with a concentration of 1,000 mg/L, the solution was used as a feed for the SCWO experiments. Hydrogen peroxide (H_2O_2, 30 wt%, Junsei Chemical Co. Ltd.) was used as an oxidant. The experiments were performed in a batch-type SCWO reactor made of Hastelloy C-276. The reactor volume was 588 cm^3 (6.5 cm i.d., 9.0 cm o.d. and 17.72 cm length).

1. Corrosion Tests of Alloys in the SCWO Condition

For the corrosion test of alloys in SCWO condition, Titanium Gr7, Inconel 601, Inconel 625, Inconel 825 and Nickel were selected

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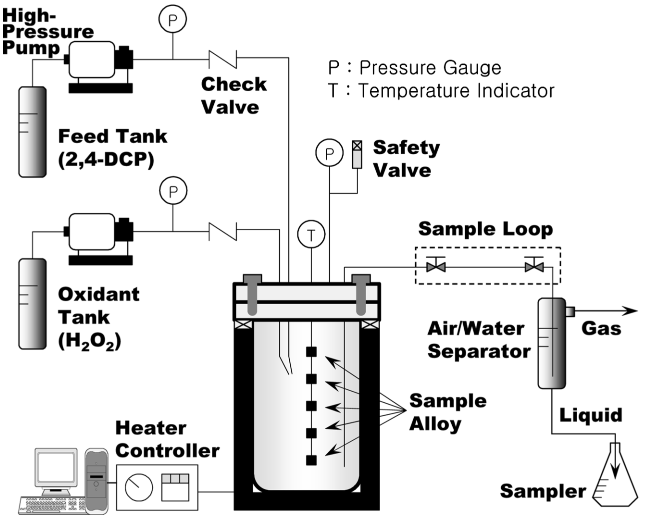


Fig. 1. Schematic diagram of SCWO process.

as corrosion-resistant metals. The alloys were prepared as coupons with a length of 10 mm, a width of 10 mm and a thickness between 1 mm and 10 mm. The coupons of all the alloys were exposed at the same condition of 1,000 mg/L of 2,4-Dichlorophenol (2,4-DCP), 400 °C, 250 bar, and 300% stoichiometric amount of H_2O_2 in a Hastelloy C-276 batch reactor.

The experimental apparatus for corrosion of alloys in SCWO is shown in Fig. 1. The apparatus consists of two high pressure syringe pumps (Lab alliance prep. 100) to feed 2,4-DCP and H_2O_2, a reactor and a pressure relief valve, all connected by high-pressure stainless steel tubing and fittings. At first, the alloy coupons were installed inside the reactor. Then, a decided amount of water with 2,4-DCP of 1,000 mg/L was fed to the reactor. It takes about 1 to 2 hours to reach the desired SCW condition. After that, the oxidizing agent, 300% stoichiometric amount of H_2O_2, was fed in to the reactor. After 10 to 15 hour-SCWO reaction, the coupons were taken out from the reactor and their surfaces were investigated by a microscope.

2. Effect of NaOH on pH and Conversion Rate

Neutralizers such as NaOH are widely applied to the SCWO process to prevent corrosion problems. The theoretical amount of NaOH for the complete neutralization was calculated under the assumption of complete oxidation of 2,4-DCP in SCW. The experimental amount of NaOH for the complete neutralization was compared with the theoretical amount of NaOH.

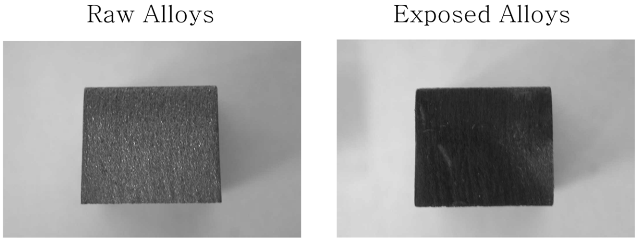
The effect of pre-dosed NaOH on the pH and conversion rate in SCWO was also investigated. To find out the effect of pre-dosed NaOH on the pH, 100% to 700% stoichiometric amounts of NaOH were pre-dosed, respectively, in the SCWO reactor filled with 1,000 mg/L of 2,4-DCP. The pH of the effluent was measured by a pH meter (Orion 420A+, Thermo Electron Corporation). The reaction time of all the SCWO experiments was 5 minutes.

The effect of NaOH pre-dosage on the conversion rate of 2,4-DCP in SCWO was examined at the conditions of 200% and 600% NaOH. After 200% or 600% NaOH was put into the reactor, 2,4-DCP was added into the reactor. After the reaction condition reached the desired SCW condition, 300% stoichiometric amount of H_2O_2 was fed into the reactor for the SCWO. The effluent samples were periodically collected through the sample loop. Each collected effluent was filtered by MFS-13 filter paper (0.5 μm, D-13 mm, ADVANTEC MFS, Inc) to eliminate particles.

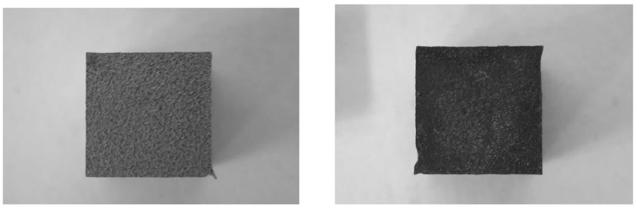
A GC/FID (5980 series 2, HP) with a capillary column (HP-1) was used to analyze decomposition efficiency. The oven operating temperature was set at 150 °C and the injection temperature was set at 300 °C. Helium was used as a carrier gas at a 1 ml/min flow rate.

RESULTS AND DISCUSSION

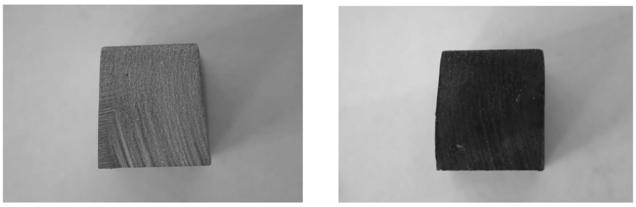
1. Corrosion Tests of Alloys in the SCWO Condition



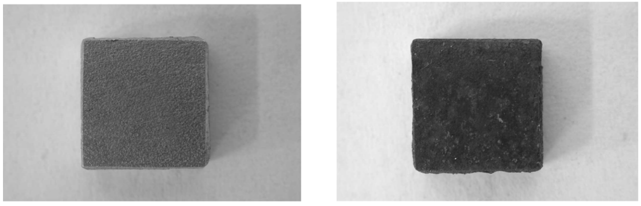
Titanium Gr 7



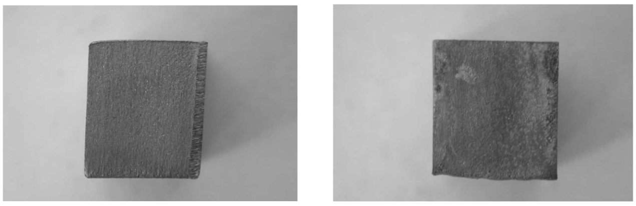
Inconel 601



Inconel 625



Inconel 825



Nickel

Fig. 2. Comparison of microscopic surface between raw and exposed alloys at 1,000 mg/L of 2,4-DCP, 250 bar and 400 °C.

The corrosion phenomena on the surface of alloys were studied at the condition of halogenated hydrocarbon oxidation in SCW. The five alloys were simultaneously exposed at SCW condition of 250 bar and 400 °C with 2,4-DCP of 1,000 mg/L and H_2O_2 of 300% stoichiometry.

Fig. 2 shows the microscopic images of the alloys before and after the corrosion test. After the corrosion test, the surface morphologies of all the alloys were changed significantly even though the degree of change was different among the alloys. Corrosion phenomena occurred by electrolyte dissociation and water density, as influenced by temperature and pressure, upon the kinetics of corrosion of metals and alloys in supercritical water. The corrosion process at near-critical temperatures is believed to involve acid attack, with the concentration of H^+ being a function of the dissociation constant of HCl, which is a major product of the oxidation of chlorinated organic waste, and of the density of the solution [Kriksunov and Macdonald, 1995].

In Fig. 2, the surface of all the tested alloys seems to be covered by carbon-contaminated layer due to the change of color except for Nickel. The difference of corrosion level among the tested Inconels implies that the corrosion in the SCWO can be significantly affected by the amount of constituent element of alloy. Titanium Gr7 also showed a color change with corrosion. Therefore, it is concluded that the surface of the alloys is corroded at the SCWO of halogenated compounds and is involved in the hydrocarbon decomposition.

It is noted that the corroded color of Nickel itself is different from that of Inconel even though the Inconels are Ni-based alloys. The surface of the Nickel only shows Ni-depletion. It implies that the carbon deposition on the surface is related to the other metal elements in the alloys instead of Ni.

From the above results, it is found that any tested metal alloys cannot resist the corrosion phenomena in the SCWO of halogenated compounds. As a result, a study on the application of neutralizer is needed to protect SCWO system from the corrosion.

2. NaOH Neutralization of Effluent from SCWO Process

In the SCWO process, the protection of effluent parts from the corrosion is as important as that of the reactor itself. In this study, the theoretical amount of NaOH for the complete neutralization of effluent was compared to the experimental result in the SCWO.

The theoretical amount of NaOH for the complete neutralization was calculated under the assumption of complete decomposition of 2,4-DCP in the SCWO as follows: $C_6H_4Cl_2O+12H_2O_2\rightarrow 6CO_2+2HCl+13H_2O$.

Fig. 3 shows the relationship between theoretical pH variation and NaOH dosage amount according to the decomposition of 2,4-DCP. After the pH of the decomposed effluent was steeply decreased to about 3 at the low concentration of 2,4-DCP, the pH was gradually decreased with an increase in 2,4-DCP concentration. On the contrary, the needed amount of NaOH showed a unfavorable shape with an increase in 2,4-DCP concentration. When the concentration of 2,4-DCP was 1,000 mg/L, the theoretical pH by the complete oxidation was about 2.21 and the corresponding amount of NaOH for the complete neutralization was 0.247 g/L.

Since the effluent would be discharged at sub-critical condition, 200% NaOH is enough to protect the discharge part of system from the corrosion. However, as mentioned before, an excess amount of NaOH is needed to protect the reactor at supercritical condition from corrosion because of low solubility of salt at SCW. Therefore, the various excess amounts of NaOH with 2,4-DCP concentration were presented in Fig. 3. And the results were used in the experiments for the NaOH pre-dosage in the SCWO.

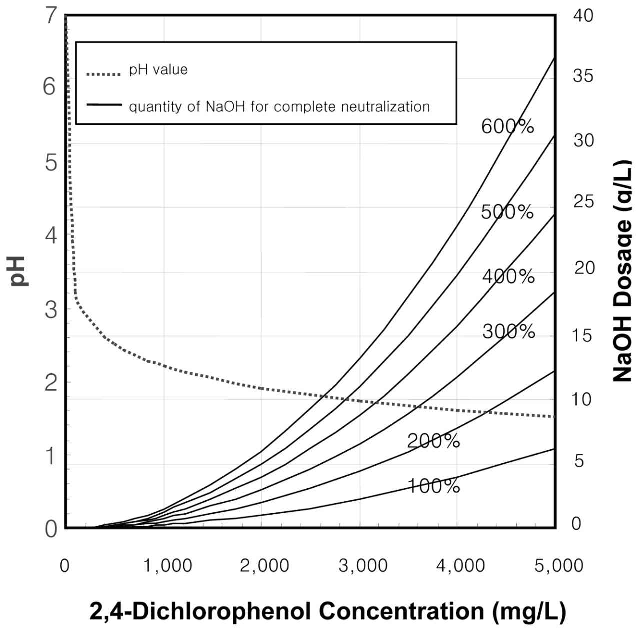


Fig. 3. pH variation and NaOH dosage amount with 2,4-DCP.

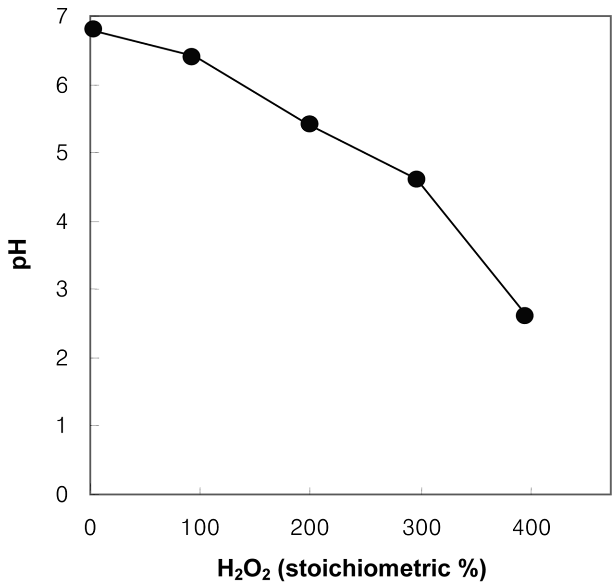


Fig. 4. pH variation with oxidants.

Fig. 4 shows the effect of the amount of oxidant on the pH of the effluent. When no oxidant was added to the reactor, the pH value was slightly less than 7. It implies that the effect on the thermal degradation of 2,4-DCP is not significant because the more degradation indicates a lower pH in the SCWO of chlorinated carbon [Kritzer et al., 1999].

Although H_2O_2 of 100% stoichiometry was injected into the reactor, the variation of pH was not significant. It means that the theoretical amount of oxidant cannot perform the complete oxidation of 2,4-DCP. The oxidant supplied to the reaction seems to be used to form metal oxide film on the surface of the alloy rather than used to the decomposition of 2,4-DCP [Lee et al., 2006]. When H_2O_2 of 400% stoichiometry was injected in the reactor, the pH value was similar to that of the complete oxidation reaction. This suggests that more than 99% of conversion rate can be achieved when H_2O_2 of 400% stoichiometry is added to the decomposition reaction of 2,4-DCP in SCWO.

Fig. 5 shows the amount of NaOH to neutralize the effluent obtained from the SCWO of 2,4-DCP with H_2O_2 of 400% stoichiometry. To neutralize the effluent to the pH of 7, 14 mg/L of NaOH should be added to the discharged line.

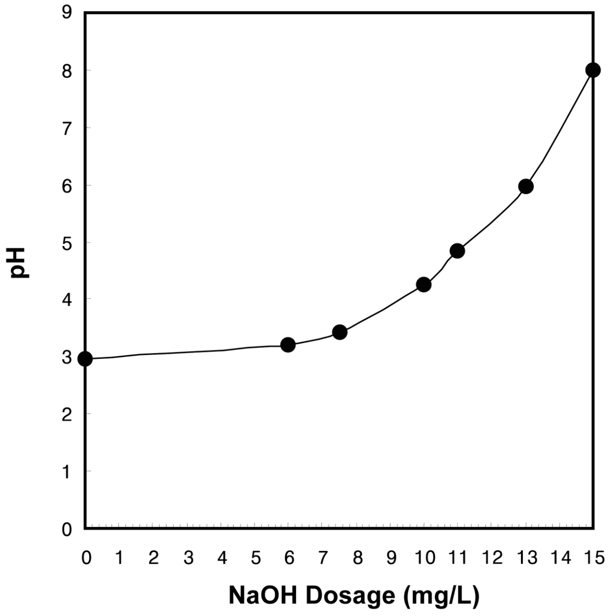


Fig. 5. Amount of 400% NaOH for neutralization of effluent.

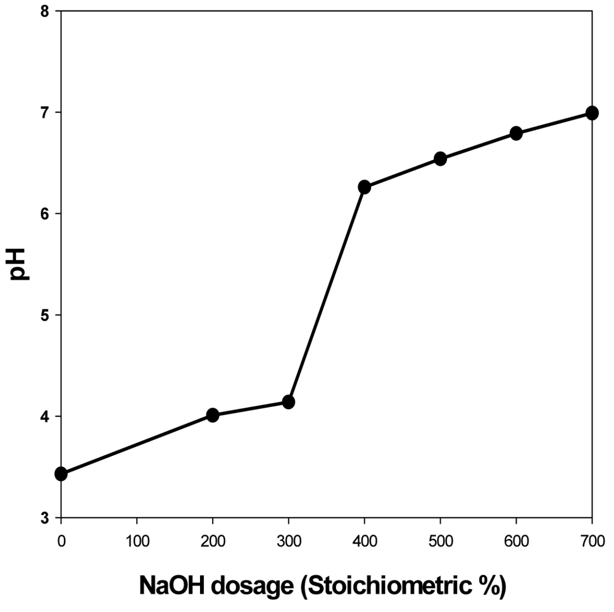


Fig. 6. pH variation with excess of NaOH pre-dosage at 1,000 mg/L of 2,4-DCP, 250 bar and 400 °C.

3. Effect of Pre-dosed NaOH on the pH Value and Conversion Rate

Fig. 6 shows the pH value of the effluent from the SCWO of 2,4-DCP at H_2O_2 of 400% stoichiometry when the 100-700% stoichiometric amount of NaOH are added to the reactor, respectively.

The addition of 100-300% stoichiometric amounts of pre-dosed NaOH could not give any significant effect on the variation of pH. It indicates that certain amount of NaOH at 300% stoichiometric amount does not participate in the neutralization reaction. It rather seems to contribute to participate in other reactions such as ring opening reaction of intermediates or substitution reaction of 2,4-DCP so that it increases the decomposition rate of 2,4-DCP. It is suggested that the hydroxide ions serve as nucleophilic reagents and activate electron withdrawing groups in the supercritical water. Therefore, a substitution reaction occurs between halogenated hydrocarbon and hydroxide ions [Lee et al., 2002]. It is expected that the ring opening reaction of chlorinated aromatic compounds by the decomposition reaction at high temperatures and high NaOH concentrations occurs in the supercritical water. As a result, the pH of effluent was significantly increased after certain excess amount of NaOH was added in the reactor.

Fig. 7 shows the effect of pre-dosed NaOH on the conversion rate of 2,4-DCP in the SCW without the oxidant. The more pre-dosed NaOH amount led to the higher conversion rate. The conversion rate recorded over 99% when 800% of NaOH was pre-dosed into the reactor. This result also implies that the pre-dosed NaOH contributes to improve the conversion rate of 2,4-DCP in SCW.

Fig. 8 shows the conversion rate of 2,4-DCP at 400% stoichiometric amount of H_2O_2 with time when 200% and 600% of NaOH are pre-dosed into the SCWO reactor. The conversion rate of 2,4-DCP was over 95 % in one minute at 200% of pre-dosed NaOH while that of 2,4-DCP was 99.9% at the same period at 600% of pre-dosed NaOH. It can be confirmed that the pre-dosed NaOH contributes to the decomposition reaction in the SCWO. From Figs. 7

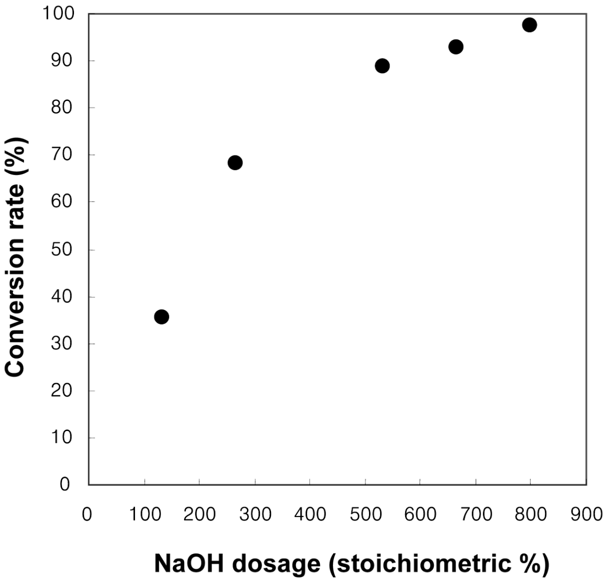


Fig. 7. Conversion variation of 2,4-DCP with NaOH pre-dosage and without H_2O_2 at 1,000 mg/L of 2,4-DCP, 250 bar and 400 °C.

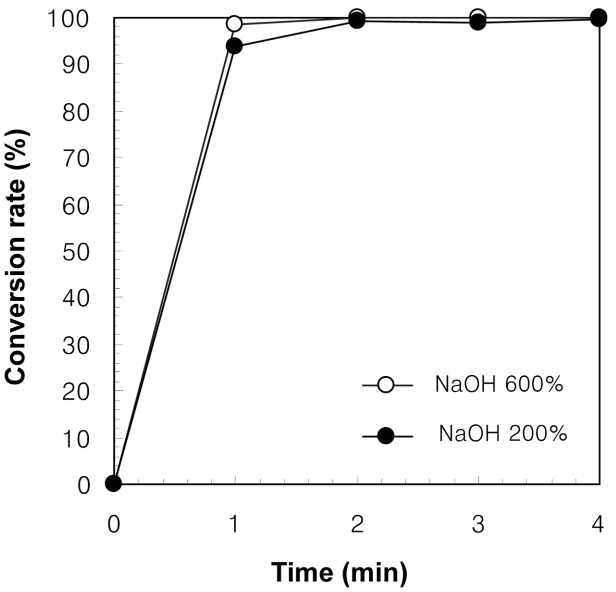


Fig. 8. Conversion variation with residence time at pre-dosage of NaOH and 400% H_2O_2.

and 8, it can be confirmed that the pre-dosed NaOH contributes to the decomposition reaction in the SCWO as mentioned in Fig. 6.

The addition of excess amount of neutralizer to SCWO reactor cannot be a complete solution of corrosion problem because it leads to a fouling/clogging problem in the system. To overcome both corrosion and fouling problems in the SCWO system for halogenated compounds, the anti-corrosive and anti-fouling reactor system should be used [Lee et al., 2005]. However, the results of this study can contribute to protect the inlet and outlet parts of the SCWO system from the corrosion because these parts are operated at the subcritical condition.

CONCLUSION

The corrosion phenomena on the surface of alloys were studied at the condition of halogenated hydrocarbon oxidation in SCW. The five alloys, such as Titanium Gr7, Inconel 601, Inconel 625, Inconel 825 and Nickel, were simultaneously exposed at SCW condition of 250 bar and 400 °C with 2,4-DCP of 1,000 mg/L and H_2O_2 of 300% stoichiometry. After the corrosion test, the surface morphologies of all the alloys were significantly changed even though the degree of change was different among the alloys. This indicates that alloys known for the high resistance to corrosion are easily corroded in the SCWO of halogenated hydrocarbons.

To prevent corrosion phenomena from the SCWO of halogenated hydrocarbon, the effect of NaOH pre-dosage, as neutralizer, on the pH value and conversion rate of SCWO of 2,4-DCP was studied.

The effluent at subcritical condition could be easily neutralized by using NaOH while the addition of 100% stoichiometric amount of pre-dosed NaOH at the SCWO reactor could not give any effect on the variation of pH significantly. To reach the pH of 7, 700% of NaOH was needed to be pre-dosed to the reactor. It was found that the more pre-dosed NaOH led to the higher conversion rate even without the oxidant. Furthermore, the pre-dosed NaOH played an important role in the SCWO of 2,4-DCP with oxidant. The more pre-dosage of NaOH contributed to improved the conversion rate of 2,4-DCP in the SCWO process.

These results indicate that the usage of neutralizer, NaOH, affects not only the pH control but also the conversion rate of 2,4-DCP in the SCWO process positively. However, the exact mechanism of reaction in the SCW condition is not revealed yet and there still exist technical problems such as fouling phenomena.

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