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Supercritical water oxidation of polyvinyl alcohol and desizing wastewater: Influence of NaOH on the organic decomposition

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Abstract

Polyvinyl alcohol is a refractory compound widely used in industry. Here we report supercritical water oxidation of polyvinyl alcohol solution and desizing wastewater with and without sodium hydroxide addition. However, it is difficult to implement complete degradation of organics even though polyvinyl alcohol can readily crack under supercritical water treatment. Sodium hydroxide had a significant catalytic effect during the supercritical water oxidation of polyvinyl alcohol. It appears that the OH^- ion participated in the C–C bond cleavage of polyvinyl alcohol molecules, the CO_2-capture reaction and the neutralization of intermediate organic acids, promoting the overall reactions moving in the forward direction. Acetaldehyde was a typical intermediate product during reaction. For supercritical water oxidation of desizing wastewater, a high destruction rate (98.25%) based on total organic carbon was achieved. In addition, cases where initial wastewater was alkaline were favorable for supercritical water oxidation treatment, but salt precipitation and blockage issues arising during the process need to be taken into account seriously.

Key words: supercritical water oxidation; polyvinyl alcohol; sodium hydroxide; catalysis; desizing wastewater

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Introduction

Polyvinyl alcohol (PVA) is a well-known water-soluble polymer (Oh et al., 2009; Wang et al., 2010; Chou, 2010). It is frequently used in the textile industry as a sizing agent, with typical chemical oxygen demand (COD) values between 10,000 and 40,000 mg O_2/L. In addition, PVA is widely used in the adhesive, emulsion paint, paper coating, and detergent-based industries and in the pharmaceutical industry as an ophthalmic lubricant. It is estimated that the global production of PVA can reach up to 650,000 tons/year (Zhang et al., 2005). Large amounts of PVA discharged from industries to the natural environment cause a series of ecological problems. PVA is harmful to human health since it accumulates in the human body through the food chain. Moreover, PVA can lead to environmental issues due to its ability to mobilize heavy metal from sediments in lakes and water streams (Chou et al., 2010; Hsu et al., 2011). However, conventional biological technologies cannot effectively break down PVA, which is attributed to the restricted degradation capacity of most microorganisms for PVA. Furthermore, a great deal of

foam is formed during the biological degradation of PVA wastewater, which adversely affects the stability of operation, and makes it difficult to achieve the desired treatment results (Chou et al., 2010). Other technologies treating PVA wastewater, such as wet air oxidation, photocatalytic degradation, direct oxidation, and electro-coagulation, can only degrade the PVA into smaller molecules to improve the biodegradability of wastewater, but are unable to achieve its complete degradation to harmless products such as carbon dioxide and water (Oh et al., 2009; Chou et al., 2010a, 2010b; Wang et al., 2010; Chou, 2010; Hsu et al., 2011). Therefore, an effective and promising treatment method for PVA wastewater is needed.

Supercritical water oxidation (SCWO) is the most potent technology for treating organic wastewaters (Veriansyah et al., 2005, 2007; Lee et al., 2006; Hayashi et al., 2007; Onwudili and Williams, 2007; Sánchez-Oneto et al., 2007). Supercritical water (SCW, T_c = 374°C, P_c = 22.1 MPa) can provide a homogeneous environment for oxidation reactions with a very low dielectric constant, eliminating interfacial mass and heat transfer limitations. In addition, the low viscosity and high diffusion coefficient make SCW a favorable medium to support very fast reaction. SCWO degradation mechanisms for many model

organic compounds and industrial wastewaters have been extensively discussed in recent years (Lee et al., 2005; Bermejo et al., 2008; Gong and Duan, 2010). A number of investigators have suggested that SCWO is a promising technology for converting most organic compounds to final products, such as water, carbon dioxide and molecular nitrogen, which are environmentally acceptable and can be released in nature without post-treatment, at a short residence time.

Much industrial wastewater, such as effluent from the paper industry, leather industry, and some chemical industries, is alkaline in nature. The desizing wastewater containing PVA is also an alkaline wastewater. Hydroxide ions have proved to be an effective catalyst for the SCWO decomposition of many varieties of organics (Lee et al., 2002; Son et al., 2006; Sun et al., 2007). Lee et al. (2002) suggested that the addition of sodium hydroxide accelerates the degradation of 2-chlorophenol and phenol under SCWO conditions, which is confirmed by the reduction of intermediate products and the increase in organics removal efficiency. Son et al. (2006) studied the effect of pre-dosed sodium hydroxide on the conversion rate of 2, 4-dichlorophenol during the SCWO reaction process. They speculated that the SCWO catalytic mechanism of hydroxide ions is that OH^- serves as a nucleophilic reagent, activating electron withdrawing groups, and is involved in the ring-opening reaction of intermediate compounds. Moreover, the catalytic effect of potassium hydroxide on the gasification of PVA in SCW has also been investigated. Yan et al. (2007) reported that the presence of OH^- effectively promotes the water-gas shift reaction and accelerates the decomposition of the PVA compounds in SCW. However, little attention has been paid to the SCWO decomposition of PVA wastewater.

In the present investigation, we performed experiments on the decomposition of PVA solution under supercritical water gasification (SCWG) and SCWO conditions respectively, with respect to various PVA solution concentrations and temperatures with or without NaOH. The reaction path of PVA during the SCWO environment is discussed based on the experimental results. In addition, the SCWO catalytic mechanism of NaOH, as another innovation of this article, was evaluated. Finally, experimental research on the SCWO treatment of PVA-containing desizing wastewater was conducted, which involved three process parameters (temperature, oxidant coefficient and reaction pH). The results of this study should be useful and beneficial for the application of SCWO technology in PVA wastewater treatment.

1 Experimental

1.1 Materials

PVA (purity ⩾ 85.0%) with a hydrolysis degree of 99.8%–100% was obtained from Tianjin Kermel Chem-

ical Reagent Company. The concentrations of the PVA solutions used in this work were 0.2 wt% and 0.5 wt%. Solutions were prepared by dissolving a certain amount of PVA in deionized water. NaOH (purity ⩾ 96%), which serves as a catalyst, was added into the PVA solution with different concentrations to investigate its role. The desizing wastewater was collected from a local dyeing plant in Shanxi Province, China. The physicochemical properties for the wastewater were as follows: COD 15,400 mg O_2/L, TOC 6024.3 mg/L, NH_4-N 47.3 mg/L, Cl^- 239 mg/L, pH 12.83, and PVA 991.9 mg/L. Hydrogen peroxide (30 wt% aqueous solution) obtained from Tianjin Fuchen Chemical Agent Company was used as the oxidant for the wastewater treatment.

1.2 Apparatus and procedures

Two experimental setups involving a continuous-flow reactor and a batch reactor were employed for degradation experiments of the PVA solution and desizing wastewater, respectively.

The continuous-flow SCWO experimental apparatus including a tubular reactor is schematically illustrated in **Fig. 1**. This system consisted of two parallel sets of feed lines: one for transferring organic solution, and the other for the oxygen, which acted as the oxidant in the degradation reaction. The tubular flow reactor (1.7 m in length and 12.3 mm in internal diameter) was made of Hastelloy C-276, whose design temperature and pressure were 600°C and 40 MPa, respectively. The organic solution preheater (1 m in length and 15 mm in internal diameter) and the reactor which were wrapped with insulating material and heated to the desired temperature by electric heating wire, controlled by a temperature regulator.
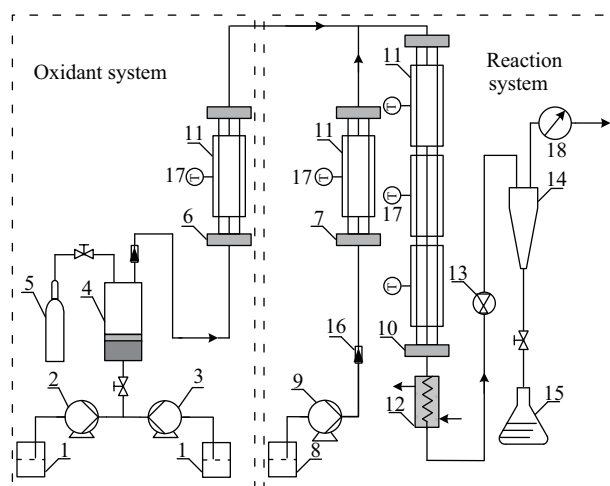
Fig. 1 Schematic diagram of tubular-flow reactor system. (1) Water tank, (2) high-pressure water pump, (3) oxidant metering pump, (4) pressure booster, (5) oxygen bottle, (6) gas heater, (7) liquid heater, (8) feed tank, (9) high-pressure feed pump, (10) tubular-flow reactor, (11) electric heater, (12) quencher, (13) back-pressure regulator, (14) gas-liquid separator, (15) liquid product collector, (16) check valve, (17) thermocouples, (18) volumetric flow meter.

Before each experimental run, the residues from previous experiments were flushed away with deionized water to minimize their possible effects on the following run. The PVA solution was pumped from the feed reservoir to the preheater and then the reactor by a high-pressure feed pump whose flow rate was controlled by a transducer. For the oxidant line, oxygen was introduced through a pressure reducer into a pressure booster at the beginning of each run, until the booster pressure rose to 5 MPa. Then distilled water was pumped from the bottom into the pressure booster by a high-pressure water pump, increasing the pressure to 30 MPa, to ensure that the upper oxygen entered into the reaction system. As soon as the reactor temperature and pressure reached the specified values, the intake valve above the booster was opened. At the same time, the high-pressure water pump was turned off and switched to an oxidant metering pump, which controlled the flow rate of the distilled water flowing into the pressure booster to regulate the flow of oxygen entering into the reaction system. The oxygen was preheated to 200°C, and its flow rate was calibrated with a volumetric flow meter before the experiments. Next oxygen was injected into a mixer before the reactor inlet and mixed with preheated organic solutions. Then, the mixture was introduced into the reactor for SCWO reaction. If the PVA solution decomposition experiment was performed under SCWG conditions, the oxidant line was shut off, and only the organic solution line was in operation. After reaction, the products were cooled down through a heat exchanger and depressurized by means of a back-pressure regulator to ambient conditions. The effluent was then released in a gas-liquid separator. The gaseous and liquid products, respectively, were collected to be analyzed.

The mixer tube above the tubular reactor, with an inner diameter of only 2 mm, could potentially bring about plugging of the mixer during the real organic wastewater experiments. Thus, we performed the desizing wastewater experiments in a batch reactor. The batch reactor system employed in this work was the same one as used in our previous study (Guo et al., 2010). Hydrogen peroxide served as the oxygen source in this reaction system. According to the temperature and pressure required in this experiment, a known volume of desizing wastewater was charged into the reactor. Before heating, the whole system was purged with nitrogen for 10 min to reduce the influence of residual oxygen in the air. Then, all the valves were closed and the reactor was heated to the final temperature. The average heating rate of the reactor was 4.07°C/min. After the temperature reached the set point, hydrogen peroxide was introduced into the reactor by a high pressure metering pump and this point was recorded as the starting point of the reaction. The system pressure was determined by the volume of the feed solution and was calculated by water physics properties software when the desired reaction temperature and pressure were given.

The volume of H_2O_2 was determined by the initial COD of the wastewater as analyzed before each run. After a certain reaction time was reached, the outlet valve was opened. The effluent was first cooled down to room temperature rapidly by passing through a heat exchanger, and then the liquid sample was collected and analyzed.

1.3 Analysis

The gaseous products were analyzed by a gas chromatograph (GC-112A) with a thermal conductivity detector (TCD), and helium was used as the carrier gas. A 3 m × 3 mm TDX-01 packed column was used and operated at the column temperature of 50°C, while the TCD detector was operated at 60°C. The method of analysis was simple and effective for the detections of H_2, CO_2, CO, CH_4, N_2 and O_2. The total organic carbon (TOC) concentrations in the liquid phase were monitored using a TOC analyzer (ET1020A). The PVA concentration in aqueous solution was determined by using a 754 UV-Vis spectrophotometer at the λ_{max} of 680 nm. The measurement was made based on the fact that PVA reacts with iodine to generate a blue-green complex in the presence of boric acid (Finley, 1961), and the complex concentration is related to the absorbance. Therefore, a calibration curve can be obtained by plotting the absorbance value as a function of PVA concentration. The identification of organic components in liquid products were performed on a GC/MS, an Agilent 6890 GC system equipped with a HP-5 column and an Agilent 5973 mass selective detector. Helium was used as carrier gas.

1.4 Calculation methods

The destruction of PVA was evaluated in terms of TOC removal (TOC_{rem}) and PVA removal (PVA_{rem}), which are defined, respectively, as shown in Eqs. (1) and (2).

$$TOC_{rem} = \frac{[TOC]_0 - [TOC]_f}{[TOC]_0} \times 100\% \quad (1)$$

$$PVA_{rem} = \frac{[PVA]_0 - [PVA]_f}{[PVA]_0} \times 100\% \quad (2)$$

where, $[TOC]_0$ and $[PVA]_0$ are the initial concentration of TOC and PVA for organic solutions, while $[TOC]_f$ and $[PVA]_f$ are the residual concentrations in liquid products.

For the PVA solution experiments, the oxygen level was determined based on the oxidant coefficient of 250% and the assumption of complete conversion of PVA:

$$(C_2H_4O)_n + \frac{3}{2}nO_2 \longrightarrow 2nCO_2 + 2nH_2O \quad (3)$$
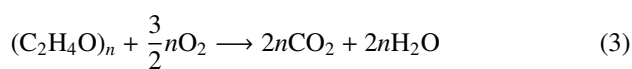
During the continuous-flow experiments, residence time was calculated from Eq. (2):

$$t = (\frac{V_r}{Q_0}) \times (\frac{V_0}{V}) \quad (4)$$

where, V_r (0.2 L) is the reactor volume, Q_0 and V_0 are the volumetric flow rate and specific volume of liquid

effluent under room temperature and atmospheric pressure conditions, respectively. V is the specific volume of feed solution under reaction conditions, which can be obtained with calculation software for water physics properties (approximate evaluation under low organic concentrations) when reaction temperature and pressure are given. By changing the flow rate of the feed pump corresponding to the density of water at each temperature, the residence time for all runs was maintained at 30 sec.

With respect to the SCWO degradation of the desizing wastewater, the oxidant coefficient ($[O_2]_{ceo}$) is expressed as Eq. (5).

$$[O_2]_{ceo} = \frac{[O_2]_0}{[COD]_0} \times 100\% \qquad (5)$$

where, $[O_2]_0$ (mg/L) is the oxidant concentration, and $[COD]_0$ is the initial COD content of the desizing wastewater. Additionally, the reaction time for desizing wastewater experiments in the batch reactor was explained in Section 2.2, and was constant at 30 sec in the batch reactor experiments.

2 Results and discussion

2.1 Degradation of PVA

All experiments for PVA degradation were performed at 25 ± 1 MPa in a continuous tubular reactor system as a function of reaction temperature, initial PVA concentration and NaOH addition, with or without oxidant. The oxidation coefficients involved in the SCWO experiments were kept constant at 250%.

Figure 2 shows the TOC and PVA removals as a function of temperature ranging from 320°C to 550°C with two PVA concentrations of 0.5 wt% and 0.2 wt%, in the absence of NaOH. As seen from **Fig. 2a**, the PVA completely disappeared regardless of the addition of oxidant, and PVA removals were as high as 99%. However, the

TOC was significantly lower than that of PVA, ranging from 74.3%–85.1% and 93.5%–98.1% under SCWG and SCWO conditions, respectively. The results indicate that in the above SCW situation PVA can be easily decomposed to smaller molecules, which were relatively difficult to completely degrade. This consistent fact could also be obtained from **Fig. 2b** for PVA concentration of 0.2 wt%. TOC removal at SCWO conditions was obviously higher than that for SCWG, implying that the SCWO reactions can ensure the effective decomposition and complete degradation of PVA organics. Comparing **Fig. 2a** with **b**, we can observe that, under the same reaction conditions, the organic destruction efficiency for the 0.5 wt% PVA solution was always higher than that for the 0.2 wt% PVA solution. This fact demonstrates that the removal efficiency increased with the reactant concentration during the SCWG and SCWO reactions for PVA organic solutions, which can also be found from exponential reaction kinetic equations.

Figures 3 and **4** illustrate the distribution of gas and liquid products for the PVA degradation reaction under SCWG and SCWO conditions. As is evident from **Fig. 3**, at 25 MPa, 510°C and 550°C, the gaseous products in the case of SCWG reaction of PVA included H_2, CO, CH_4 and CO_2. It is evident that the molar fraction of H_2 and CO declined, while CH_4 and CO_2 increased, as the temperature rose from 510°C to 550°C. This is because under these conditions, PVA underwent SCWG reaction. The increase of temperature accelerated the methanation reaction, which consumed H_2 and CO and induced the increase of CH_4. Furthermore, along with the introduction of oxygen into the reaction system, there was no CH_4 formed during the SCWO process and the H_2 fraction significantly decreased, while CO and CO_2 fractions increased. Under SCWO conditions with the temperature elevated from 510°C to 550°C, the CO content decreased and CO_2 increased, implying that an increase in temperature accelerated the complete degradation of smaller
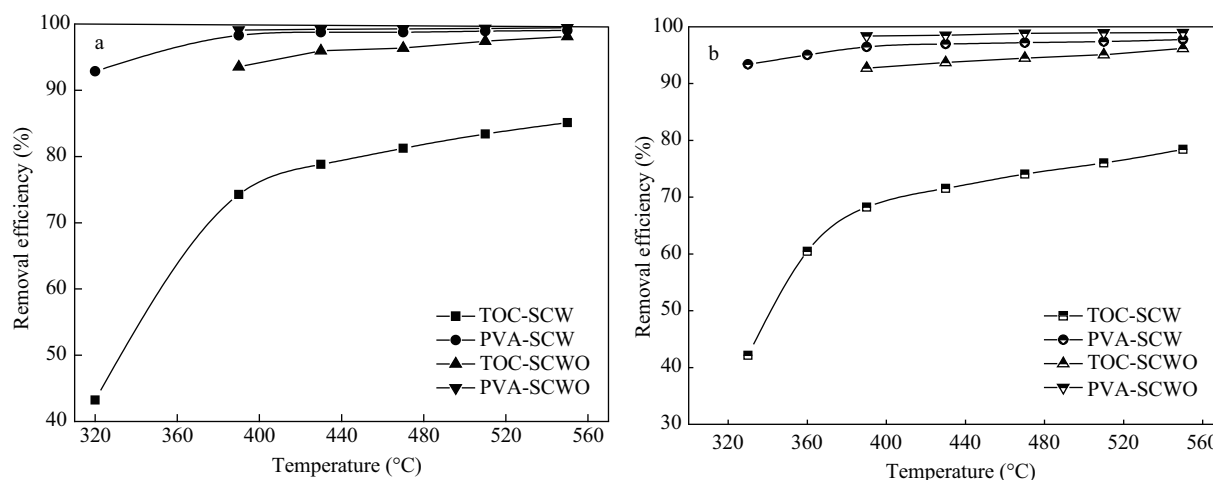

Fig. 2 Experiment results for TOC and PVA removals as a function of temperature under SCWG and SCWO with initial PVA concentration of 0.5 wt% (a) and 0.2 wt% (b).
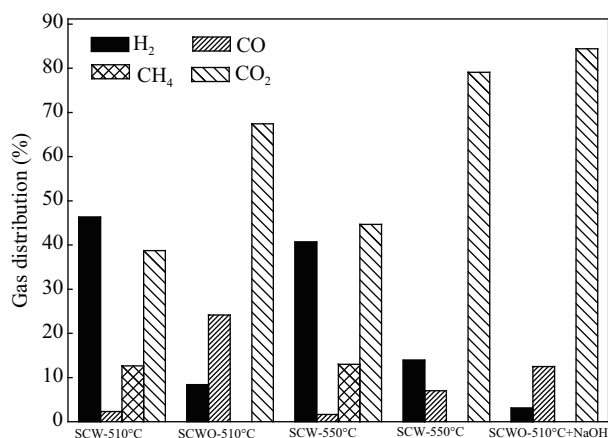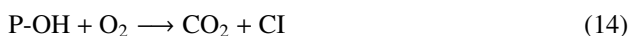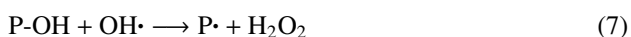
Fig. 3 Gaseous products during the PVA degradation process under SCWG and SCWO.

intermediated compounds. This can also been confirmed by the observation that elevating temperature led to a dramatic increase in TOC removal, as demonstrated in **Fig. 2**. As displayed in **Fig. 4b**, during the SCWO reaction for the PVA solution at 510°C, 25 MPa, formic acid, oxalic acid, pentadecanoic acid, hexadecanoic acid, octadecanoic acid, octanal, 2-heptanol, eicosane, and cyclohexane were produced.

Several researchers (Henrikson et al., 2003; Anitescu et al., 2005; Ploeger et al., 2006a, 2006b; Hayashi et al., 2007) have reported that the SCWO destruction of organic compounds occurs primarily through free radical pathways rather than the ionic pathways that dominate in liquid water. This is because SCW acts as a nonpolar solvent with a low dielectric constant (Loppinet-Serani et al., 2008). Based on the above discussion, we speculated the reaction scheme for the SCWO decomposition of PVA, as shown in the following:

$$O_2 + H_2O \longrightarrow \cdot OH + HO_2 \cdot \tag{6}$$

$$P\text{-}OH + OH \cdot \longrightarrow P \cdot + H_2O_2 \tag{7}$$

$$H_2O_2 \longrightarrow 2 \cdot OH \tag{8}$$

$$H_2O_2 \longrightarrow H \cdot + \cdot OOH \tag{9}$$

$$H \cdot + H \cdot \longrightarrow H_2 \tag{10}$$

$$P \cdot + O_2 \longrightarrow P\text{-}OO \cdot \tag{11}$$

$$P\text{-}OO \cdot + H \cdot \longrightarrow PO \cdot + \cdot OH \tag{12}$$

$$P{=}O \longrightarrow CO + CI \tag{13}$$

$$P\text{-}OH + O_2 \longrightarrow CO_2 + CI \tag{14}$$

$$CO \longrightarrow CI \tag{15}$$

$$CI \longrightarrow CO_2 \tag{16}$$

$$CO \longrightarrow CO_2 \tag{17}$$

During the SCWO process of the PVA solution, first, the PVA compounds were broken into smaller molecules P-OH. Then most of the P-OH was attacked by HO· resulting

in the loss of -OH, and the rest was oxidized by O_2 to CO_2 and CI, which represents a carbon-containing intermediate in the pathway between CO and CO_2. In a series of reaction paths, Reaction (10) represents a limiting step, whose conversion controls the overall degradation. Reactions (12) and (13) stand for the water-gas shift reactions, explaining the production of H_2 during the SCWO process of PVA. Reaction (14) represents the complete oxidation of CO to CO_2.

Finally, as shown in **Fig. 2**, in the environment of subcritical water at 320°C–360°C, 25 MPa, PVA removal ranged from 92.9% to 95.0%, while TOC removal ranged from 43.2% to 60.4%, which were much lower than in SCW. Moreover, no gas was collected during these experiments, and this phenomenon occurred until the temperature rose to 470°C, with the absence of oxygen. A possible explanation for this phenomenon can be attributed to undesired char formation in the dehydration reaction.

2.2 Effect of NaOH on SCWO of PVA

Figure 5 displays the influence of the NaOH concentration on the SCWO destruction for the PVA solution at 510°C, 25 ± 1 MPa. It can be observed that as the addition of NaOH increased from 0 wt% up to 0.20 wt%, not only could the TOC removal be boosted from 95.1% to 99.1%, but the PVA could achieve complete decomposition as well. It appears that the addition of NaOH into the feed was conducive to the cleavage of PVA molecules, and meanwhile, accelerated the complete oxidation of organics.

The OH^- ion helped the PVA break into smaller molecules. We assume that the catalytic reactions in the presence of OH^- proceeded as follows:

$$\tag{18}$$

$$\tag{19}$$

$$\tag{20}$$

$$\tag{21}$$
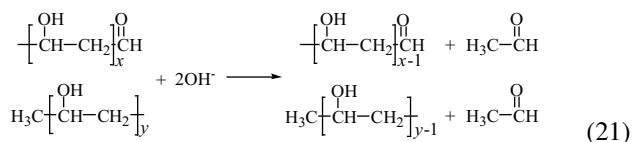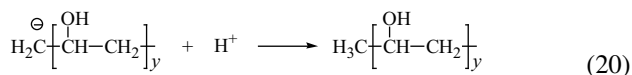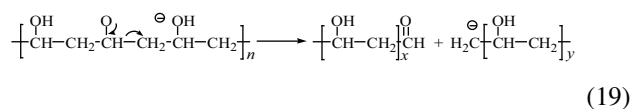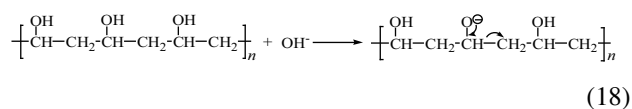
In Reaction (18), the OH^- ion captured a proton from hydroxyl, converting to water. Meanwhile, an anion intermediate formed during this reaction. Then, the intermediate was broken up to P_x-CHO and another carbanion P_y-CH_2^-, as shown in Reaction (19), while x and y are

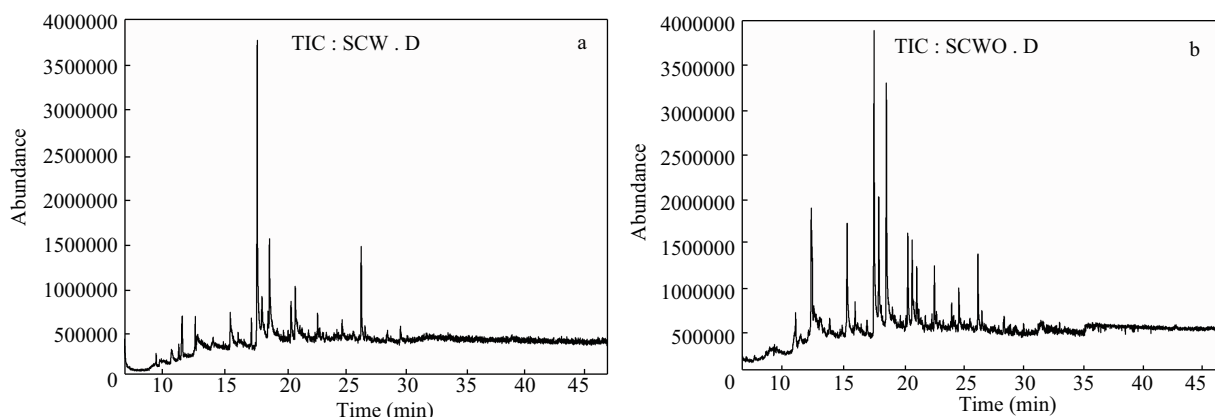**Fig. 4** GC/MS chromatograms for some intermediate compounds obtained during the decomposition of PVA at 510°C, 25 MPa. (a) under SCWG: eicosane at 15.112 min; methoxyacetic acid at 15.289 min; *n*-hexadecanoic acid at 18.815 min; isopropyl palmitate at 18.707; 11-hexadecenoic acid at 19.450 min; octadecanoic acid at 20.890 min; oxalic acid at 21.421 min; cycloheptane at 21.936 min; 2-dodecanol at 22.484 min; cyclohexane at 22.559 min, (b) under SCWO: octanal at 14.234 min; hexadecanoic acid at 17.244 min; pentadecanoic acid at 17.815 min; isopropyl palmitate at 18.798 min; 2-heptanol at 19.433 min; formic acid at 19.735 min; eicosane at 19.936 min; octadecanoic acid at 20.879 min; oxalic acid at 21.416 min; octadecyl ester at 21.582 min; cyclohexane at 23.976 min.

the polymerization degree of the organics. Followed by Reaction (19), the carbanion attracted a proton from water, forming P_y-CH$_3$ (P represented the monomer $\begin{array}{c}-\text{CH}-\text{CH}_2-\\ |\\ \text{OH}\end{array}$), and simultaneously released one OH$^-$ ion. As Reaction (21) displays, P_x-CHO and P_y-CH$_3$ combined with OH$^-$ ions again, repeating the above reaction processes, in which acetaldehydes were generated in both cases, as well as other organic compounds with lower polymerization degrees, P_{x-1}-CHO and P_{y-1}-CH$_3$. This reveals that the introduction of NaOH into the feed can promote the cleavage of the C–C bond in the PVA molecule. Based on the above discussion, acetaldehyde was a typical product. Previous studies (Rice and Croiset, 2001; Onwudili and Williams, 2007) have suggested that the aldehyde compounds are the primary stable organic intermediates during the SCWO of hydroxy organics. This confirms the aforementioned hypothesis for the reaction pathway.

Figure 5 shows that NaOH had a positive influence on the complete degradation of PVA organics by the SCWO process (signified by the TOC removal). This can be attributed by the fact that OH$^-$ can promote the water-gas shift reactions (Reactions (14) and (15)) (Yan et al., 2007; Muangrat et al., 2010). Sodium hydroxide captured the CO$_2$ generated during SCWO reaction, and formed sodium carbonate. In the subsequent reaction, excess CO$_2$ was abstracted by sodium carbonate with H$_2$O and produced sodium bicarbonate, as shown in Reactions (22) and (23).

$$CO_2 + 2NaOH \rightleftharpoons Na_2CO_3 + H_2O \qquad (22)$$

$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3 \qquad (23)$$
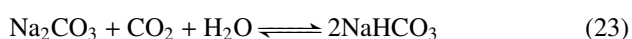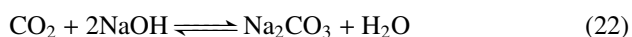
Accordingly, the reduction of CO$_2$ promoted the water-gas shift reaction equilibriums to move in the forward direction and facilitated the overall degradation process. In order to verify the assumption, we analyzed the total
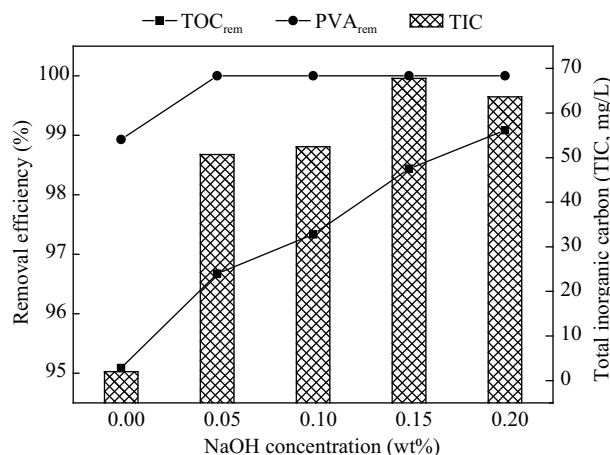
Fig. 5 Effect of NaOH on SCWO of 0.2 wt% PVA solution with an oxidation coefficient of 250% at 510°C, 25 ± 1 MPa.

inorganic carbon (TIC) of the reaction effluent for the case with and without NaOH addition in the feed, as shown in **Fig. 5**. It seems that with NaOH concentration increasing from 0.05–0.20 wt%, the TIC in liquid products significantly improved to 50.3–61.5 mg/L, relative to 1.4 mg/L without NaOH. This phenomenon is in reasonable consistency with the above predictions.

Furthermore, the effluent liquid-phase sample for the PVA SCWO reaction with 0.2 wt% NaOH was also analyzed by GC/MS. The list of identified organic acid components and their relative percent contents is shown in **Table 1**. It is clear that the percentages of acids with 0.2 wt% of NaOH were significantly lower than that of the parallel sample without NaOH. This finding can be attributed to the neutralization reaction of organic acids that were refractory during the SCWO process (Lee, 1996; Krajnc and Levec, 1997; Yu and Savage, 2000; Takahashi et al., 2012) in the presence of NaOH, and further caused an enhancement of the PVA disappearance rate. This confirms the positive effect of NaOH on PVA

Table 1   Composition of chloroform extracts from the liquid products of SCWO of PVA with and without NaOH

Identified acid compounds	Percent area (%)	
	NaOH 0 wt%	NaOH 0.20 wt%
Octadecanoic acid	11.01	7.84
Hexadecanoic acid	8.25	17.79
Pentadecanoic acid	42.33	–
Oxalic acid	1.39	1.08
Acetic acid	–	0.99

Experimental condition: 510°C, 24.5–25 MPa, $[O_2]_{ceo}$ = 2.5%, PVA = 0.5 wt%.
–: The component was not detected by GC/MS.

SCWO decomposition from another perspective.

2.3 SCWO for PVA-containing desizing wastewater

PVA is the one of the main contaminant organics in the desizing wastewater, and accounts for 50% of the COD content of the wastewater. In order to complement the above investigation, we conducted SCWO experiments for the desizing wastewater in the batch reactor experimental setup. The results with TOC and PVA removals are displayed in **Table 2**. The results show that the temperature and oxidation coefficient had positive effects on the SCWO for the desizing wastewater under the conditions of 410 –510°C and 100%–300%, respectively. At 510°C and oxidation coefficient of 250%, the TOC and PVA removals could reach 98.25% and 100%, respectively, revealing that the SCWO treatment can achieve effective destruction of organics in the desizing wastewater. The influence of the solution pH on the SCWO removal efficiency was also explored while the temperature and oxidation coefficient were kept constant at 420°C and 150%, as shown in **Table 2**. The results show that without any reagent addition, the TOC and PVA destruction efficiency was 91.56% and 95.70%, respectively. In the case when there was 0.5 wt% NaOH and the pH increased to 13.00, the TOC and PVA removals rose to 94.95% and 100%, which was consistent with the conclusion reached in Section 2.1.2 of this article.

In addition, several studies have reported the catalytic effect of OH⁻ ion on the SCWO reaction for organics. However, adjusting the initial pH value of wastewater to neutral and acidic pH by means of adding appropriate acid was detrimental to the degradation of the desizing wastewater. This is demonstrated by the reduction of both TOC and PVA removals. Thus the situation that the initial desizing wastewater was alkaline (pH = 12.83) was positively correlated with the SCWO decomposition. However, the salt deposition and blockage problems occurring during the SCWO process need to be considered seriously.

3 Conclusions

The degradation for a PVA solution used as a model compound of desizing wastewater under SCWG and SC-WO conditions was investigated in a tubular continuous reactor. Moreover, as validation, an experiment involving SCWO of the real desizing wastewater was performed in a batch reactor. The results demonstrate that SCWO destruction can achieve complete decomposition of PVA molecules in aqueous solutions, and at 550°C and oxidation coefficient of 250%, the TOC removal for the PVA solution with a concentration of 0.5 wt% could reach 98.1%. In addition, above the critical point, the organic degradation rate accelerated as the initial concentration of PVA solution increased regardless of whether or not oxidant was used. However, under subcritical conditions, PVA underwent a pyrolysis reaction, where only 43.2%– 60.4% TOC removals could be achieved, and almost no gaseous products were collected. A possible explanation for this phenomenon is attributed to the formation of char during these processes, which was disadvantageous to the preheating of the organic solution during the SCWO process. Increasing the NaOH content in the feed contributed to the improvement of the SCWO reaction. It appears that NaOH was an effective catalyst for the SCWO destruction of PVA. This is because the OH⁻ ion participated in

Table 2   Summary of the experiments for desizing wastewater[a]

Experiments	Temperature (°C)	Pressure (MPa)	$[O_2]_{ceo}$ (%)	pH	PVA$_{rem}$ (%)	TOC$_{rem}$ (%)
Temperature influence	390	22.5	250	12.83	96.71	88.05
	420	24	250	12.83	100.00	92.24
	450	24	250	12.83	100.00	94.17
	480	25.5	250	12.83	100.00	96.07
	510	26	250	12.83	100.00	98.25
Oxidant influence	449.5	28	100	12.83	97.15	84.74
	450	22.5	150	12.83	97.15	90.44
	450	22.5	200	12.83	97.15	93.41
	450	24	250	12.83	100.00	94.17
	450	23.5	300	12.83	100.00	97.51
pH value influence	420	25.5	150	12.83	95.70	89.90
	420	25.5	150	7.10	92.73	88.69
	420	25.5	150	4.12	90.94	87.99
	420	25.5	150	13.00	100	94.95

[a] Experiments were carried out in the batch reactor.

the cleavage reaction of the PVA molecules, the CO_2-capture reaction and neutralization of intermediate organic acids. Acetaldehyde was a typical intermediate product. The TIC contents for aqueous products were satisfactorily consistent with the above hypothesis. Finally, experimental results for SCWO of desizing wastewater reveal that PVA and TOC removals can reach 100% and 98.25%, respectively. Furthermore, an initial pH value of wastewater of 12.83 was found to be conducive to the SCWO treatment process. Nevertheless, salt deposition and blockage issues arising during the SCWO process need to be carefully considered to achieve the best overall degradation results.

Acknowledgments

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