Supercritical Water Oxidation of Spent Extraction Solvent Simulants (Postprint)

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Abstract

The rapid development of nuclear technology has led to more liquid organic radioactive wastes. Different from the regular aqueous radioactive wastes, these liquids possess a higher hazard potential and cannot be disposed through the conventional methods due to their radioactivity and chemical nature. Spent extraction solvent is a kind of common liquid organic radioactive wastes. In this work, tri-butyl phosphate (TBP), which is more difficult to degrade in the spent extraction solvent, was used as the model compound. Influences of reaction conditions on total organic carbon (TOC) removal and the volume percentage of each gas component under supercritical water oxidation (SCWO) were studied. The SCWO behaviors of spent extraction solvent simulants were studied under the optimal conditions derived from the TBP experiment. The SCWO experiments were studied at 400–550 ℃, oxidant stoichiometric ratio of 0–200%, feed concentration of 1.5%–4% and pressure of 25 MPa for 15–75 s. The results show that the TOC removal of the simulants was greater than 99.7% and CH4, H2 and CO were not detected at 550 ℃, 25 MPa, oxidant stoichiometric ratio of 150%, feed concentration of 3%, and residence time of 30 s.

Full Text

Preamble

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The rapid development of nuclear technology has generated increasing volumes of liquid organic radioactive waste. Unlike conventional aqueous radioactive wastes, these liquids pose higher hazards and cannot be disposed of through standard methods due to their combined radioactivity and chemical properties. Spent extraction solvent represents a common type of liquid organic radioactive waste. In this study, tri-butyl phosphate (TBP), the most recalcitrant component in spent extraction solvent, was selected as a model compound. The effects of reaction conditions on total organic carbon (TOC) removal and gas composition were investigated under supercritical water oxidation (SCWO). The SCWO behavior of spent extraction solvent simulants was then examined under optimal conditions derived from TBP experiments. Experiments were conducted at temperatures of 400–550 °C, oxidant stoichiometric ratios of 0–200%, feed concentrations of 1.5%–4%, pressure of 25 MPa, and residence times of 15–75 s. The results demonstrate that TOC removal exceeded 99.7% for the simulants, with no detectable CH_4, H_2, or CO at 550 °C, 25 MPa, 150% oxidant stoichiometric ratio, 3% feed concentration, and 30 s residence time.

Keywords: Supercritical water oxidation, Liquid organic radioactive wastes, Spent extraction solvent, TBP
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Introduction

Radioactive liquid wastes are generated from the use of radioisotopes in nuclear research centers, medical facilities, and industrial applications [1, 2]. In recent decades, the rapid development and deployment of nuclear technologies have led to increasing volumes of these wastes, which can be categorized into aqueous radioactive wastes and liquid organic radioactive wastes. Aqueous radioactive wastes can be effectively treated by conventional radioactive wastewater treatment systems, which separate the waste into two fractions: a small volume of concentrate containing the bulk of radionuclides that remains in the management system, and a large volume of low-activity effluent that can be discharged to the environment when it meets regulatory requirements [3]. In contrast, liquid organic radioactive wastes require management strategies that address both their radioactivity and their chemical composition. Since both radioactive and organic chemical components pose health and environmental risks, these wastes cannot be disposed of through conventional methods due to their chemical nature [4, 5].

To date, incineration has been considered an attractive treatment option for liquid organic radioactive wastes, capable of destroying hazardous organics while significantly reducing waste volume [6–8]. This technology is currently employed in several countries, including Canada, France, the Russian Federation, and the USA [7]. However, incineration facilities are costly to construct and operate, and they produce toxic by-products in the off-gas (e.g., furans and dioxins). Additionally, incineration requires supplemental fuel for wastes containing less than 30 wt.% organic compounds, primarily due to the high water content that must be vaporized [9]. Other problems associated with incineration include agglomeration [10] and equipment corrosion [11]. Consequently, new technologies are needed for the effective and safe disposal of these wastes.

Supercritical water oxidation (SCWO) is regarded as a promising alternative to incineration for treating hazardous industrial wastes and wastewaters, and has attracted considerable attention in recent decades [12–15]. Under supercritical conditions ($P > 22.1$ MPa and $T > 374$ °C), water exhibits unique properties including negligible surface tension, high diffusivity, low viscosity, low inorganic solubility, and high organic solubility. Supercritical water is completely miscible with oxygen, creating a homogeneous reaction medium that is ideal for oxidizing liquid organics [16–18]. Generally, organic compounds can be completely degraded within seconds without forming toxic gaseous oxides (such as SO and NO) at temperatures of 450–500 °C (compared to >1000 °C required for incineration).

Numerous practical SCWO applications have been demonstrated for treating chlorinated hydrocarbons [19], municipal sewage sludge [20], and other waste streams. It is anticipated that liquid organic radioactive wastes can be efficiently decomposed in supercritical water, leaving radioactive nuclides in the liquid effluent for subsequent treatment by conventional radioactive wastewater systems. Although SCWO faces challenges such as corrosion and plugging [21, 22], these issues can be mitigated through various approaches, including selection of corrosion-resistant reactor materials [23–25] and novel reactor designs [26]. In our SCWO facility, the reactor and pre-heater are constructed from Inconel 625, a corrosion-resistant alloy suitable for SCWO conditions [27]. New reactor designs will be developed in future work.

Spent extraction solvent is a type of liquid organic radioactive waste generated from solvent extraction research, uranium refining, and related processes. Tributyl phosphate (TBP) is the most commonly used extraction solvent, typically diluted with light saturated hydrocarbons such as n-dodecane or paraffin for extraction operations. Compared to aqueous radioactive wastes, spent extraction solvents contain organic materials with higher hazard potential due to their mobile, unstable, and flammable characteristics. Therefore, effective management of these wastes is essential to ensure safe handling, processing, storage, and disposal.

This study employs a two-step approach to extend SCWO system lifetime and minimize reactor corrosion, particularly from nitric acid. The first step involves optimization of reaction conditions for TBP, which is difficult to degrade. TBP was treated under SCWO conditions in a continuous-flow reactor to investigate the effects of reaction parameters—including oxidant stoichiometric ratio, residence time, feed concentration, and temperature—on liquid and gas products. The second step comprises SCWO experiments with spent extraction solvent simulants.

II. Materials and Methods

A. Apparatus and Procedure

The SCWO-250 system, designed and fabricated by Supercritical Fluid Technologies, Inc. (USA), is illustrated in [Figure 1: see original paper]. The system consists of a tank pre-heater (200 mL, Inconel 625) and a tank reactor (250 mL, Inconel 625), capable of operating at pressures up to 28.4 MPa and temperatures up to 600 °C. A back-pressure regulator provides precise system pressure control. Under typical operating conditions, water and oxidant (H_2O_2) flow rates range from 1-100 mL/min, while feed flow rates range from 0–36 mL/min. An online pH probe with digital display is installed before the gas-liquid separator. Front panels provide access to pressure vessels, valves, fittings, and electronics. As an additional safety precaution, two rupture disc assemblies provide mechanical overpressure protection: one installed in the piping between the water pump and pre-heater, and the other between the cooler and back-pressure regulator.

At the beginning of each experiment, the temperature and pressure of both pre-heater and reactor were raised to the desired values using deionized water. A fluid mixture of water and oxidant (H_2O_2) was first introduced into the pre-heater by a high-pressure metering pump (Pump 1). The feed solution was then introduced into the reactor by a second high-pressure metering pump (Pump 2). The reactor was heated by electrical coils wrapped around the vessel. The effluent exiting the top of the reactor was rapidly cooled after passing through the cooler and depressurized to ambient pressure via the back-pressure regulator. Temperature and pressure were controlled by a proportional integral derivative (PID) controller. The effluent was directed to a gas-liquid separator, with gas products transported to a gas chromatograph for composition analysis and liquid products sampled for analysis.

B. Materials and Analytical Methods

Tri-butyl phosphate (TBP, 98.5% purity), hydrogen peroxide (H_2O_2, 30% w/w), and nitric acid (HNO_3, 65%-68% purity) were purchased from Sinopharm Chemical Reagent Co. (China). n-Dodecane (97% purity) and di-butyl phosphate (HDBP, 97% purity) were obtained from Sigma-Aldrich Co. (Germany). Deionized water was prepared using a Milli-Q ultrapure water purification system with a 0.22-µm filter. Total organic carbon (TOC) in liquid products was analyzed using a TOC analyzer (Shimadzu TOC-L CSH, Japan). Measurements from three samples were averaged to determine TOC removal. Gas composition was determined by a gas chromatograph (Agilent GC 7890A, Agilent Technologies, Inc., USA) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID), each using a G3591-80013 Q packed column. Helium was used as carrier gas for TCD at 40 mL/min, while nitrogen was used for FID at 40 mL/min. The column, TCD detector, and FID detector were maintained at 50 °C, 250 °C, and 300 °C, respectively.

C. Feedstock

n-Dodecane is commonly used as a diluent in TBP-HNO_3 extraction systems. The typical TBP/diluent composition is 30 vol.% TBP and 70 vol.% n-dodecane, which represents a classical mixing ratio in the nuclear industry. The primary degradation products of the TBP/diluent system are HDBP formed through hydrolysis and radiolysis during fuel reprocessing. HDBP can be further hydrolyzed in the presence of HNO_3 to form H_2MBP, though the amount of H_2MBP formed is generally negligible [28]. Therefore, TBP, HDBP, n-dodecane, and HNO_3 constitute the major components of spent extraction solvent. The concentrations of HDBP and HNO_3 vary depending on the specific extraction process; mid-range values were selected for preparing the simulants, specifically 276 mg/L HDBP and 0.5 mol/L HNO_3 based on literature data [29], as shown in .

D. Calculation

The residence time (t) is related to feed rate (Q), reaction temperature, and pressure as described in Eq. (1):

$$t = (V_0/Q)(V/V_r)$$

where $V_0 = 250$ mL is the reactor volume; Q and V are the volumetric flow rate and specific volume of liquid effluent under room temperature and pressure conditions, respectively; and V_r is the specific volume of feedstock under reaction temperature and pressure.

The oxidant stoichiometric ratio is calculated using Eq. (2):

$$\text{Oxidant stoichiometric ratio} = ([\mathrm{H_2O_2}]_r/[\mathrm{H_2O_2}]_0) \times 100\%$$

where $[H_2O_2]_0$ is the concentration theoretically required for complete oxidation of organic matter according to reaction stoichiometry, and $[H_2O_2]_r$ is the actual concentration used in each experiment.

TOC removal of liquid effluent was calculated using Eq. (3):

$$\text{TOC removal} = (1 - \mathrm{TOC}_L/\mathrm{TOC}_0) \times 100\%$$

where TOC_L is the total organic carbon concentration in the liquid effluent, and TOC_0 is the total organic carbon concentration in the feedstock accounting for dilution effects of H_2O and H_2O_2, obtained through theoretical calculations. Gas product composition was determined by GC.

III. Results and Discussion

A. SCWO of TBP

All supercritical water oxidation experiments were performed at approximately 25 MPa. This section examines the effects of oxidant stoichiometric ratio, feed concentration, residence time, and temperature on TOC removal and gas product composition.

1. Effects of Oxidant Stoichiometric Ratio TBP was treated at 500 °C, 25 MPa, 3% feed concentration, 45 s residence time, and various oxidant stoichiometric ratios (0%-200%). The pre-heater was maintained at 400 °C, where H_2O_2 completely converts to O_2 [30]. As shown in [Figure 2: see original paper], TOC removal increased rapidly with oxidant stoichiometric ratio, reaching approximately 67% even without oxidant addition. This demonstrates that water plays a crucial role in chemical reactions under SCWO conditions, acting as a reactant/product in bond-breaking reactions such as hydrolysis and as a supplier of hydrogen atoms. Additionally, water generates high concentrations of H^+ and OH^- ions that significantly influence acid- or base-catalyzed reactions [31]. TOC removal values were 85%, 98%, 99.2%, and 99.5% at oxidant stoichiometric ratios of 50%, 100%, 150%, and 200%, respectively. Higher oxidant stoichiometric ratios increase $OH\cdot$ and O_2 concentrations; since $OH\cdot$ is a powerful oxidizing species [32], organic degradation increases correspondingly. Based on [Figure 2: see original paper], an oxidant stoichiometric ratio of 150% is sufficient for complete TBP decomposition, achieving over 99% TOC removal.

2. Effects of Feed Concentration The effect of TBP concentration on TOC removal at 500 °C, 25 MPa, 150% oxidant stoichiometric ratio, and 45 s residence time is presented in [Figure 3: see original paper]. Initial feed concentration appears to have only slight influence on TOC destruction efficiency. At 1.5% feed concentration, TOC removal was approximately 97%, while at concentrations $ $2%, removal exceeded 99%. SCWO demonstrates excellent processing capacity for organic compounds. At higher feed concentrations, more reaction heat is released, causing localized overheating that enhances organic degradation. The maximum TBP concentration tested in this work was 4 wt.%, which is higher than values reported in literature [33, 34] due to limitations in oxidant concentration.

3. Effects of Residence Time Organic compounds degrade rapidly under SCWO conditions [35]. [Figure 4: see original paper] shows the effect of residence time on TOC removal at 500 °C, 25 MPa, 4% feed concentration, and 150% oxidant stoichiometric ratio. Increased residence time positively influenced TOC removal in liquid products, with removal values of approximately 95% at 15 s and >99% at 30 s. The residence time effect became less significant beyond a threshold value; in this work, a residence time of approximately 30 s was considered both effective and practical.

4. Effects of Reaction Temperature Temperature is a critical parameter in SCWO of organic compounds. [Figure 5: see original paper] illustrates the temperature effect on TOC removal at 25 MPa, 4% feed concentration, 150% oxidant stoichiometric ratio, and 30 s residence time. TOC removal in liquid products increased rapidly with temperature, reaching a maximum of approximately 99.7% at 550 °C. Temperature influences organic degradation through three mechanisms: (1) the reaction rate constant increases exponentially with temperature, accelerating the reaction process [36, 37]; (2) the reaction medium density decreases with increasing temperature, reducing reactant concentrations and thus reaction rates; and (3) the effective residence time decreases with increasing temperature.

5. Effects of Oxidant Stoichiometric Ratio and Temperature on Gas Products Experiments were conducted at various temperatures (400, 450, 500, and 550 °C) and oxidant stoichiometric ratios (50%, 100%, and 150%) at 25 MPa, 30 s residence time, and 4% feed concentration. [Figure 6: see original paper] shows the volume percentages of CH_4, H_2, CO, and CO_2 (excluding O_2 and other minor gases) as functions of oxidant stoichiometric ratio. As expected, oxidant stoichiometric ratio significantly impacts gas yields: CH_4, H_2, and CO yields decreased progressively with increasing oxidant ratio, becoming undetectable at 150% oxidant stoichiometric ratio, while CO_2 yield increased steadily. The maximum volume percentages of CH_4, H_2, and CO were 9.4% at 400 °C, 6.07% at 400 °C, and 45.11% at 450 °C, respectively, at 50% oxidant stoichiometric ratio. The maximum CO_2 volume percentage reached 99.99% at 550 °C and 150% oxidant stoichiometric ratio. For 50% oxidant stoichiometric ratio, temperature significantly affected CH_4 and H_2 yields, which decreased with increasing temperature. Temperature had minimal effect on CO and CO_2 yields at 50% oxidant ratio, but the effect became pronounced at higher oxidant ratios. This behavior indicates that partial oxidation occurs at lower temperatures and oxidant levels, producing intermediates and hydrogen, while higher temperatures and oxidant levels further oxidize these intermediates to final products such as carbon dioxide and water.

B. SCWO of Spent Extraction Solvent Simulants

Under optimal conditions derived from the TBP experiments (550 °C, 25 MPa, 3% feed concentration, 150% oxidant stoichiometric ratio, and 30 s residence time), the TOC removal for spent extraction solvent simulants was $(99.77 \pm 0.02)\%$, with TOC concentrations in three replicate samples measuring 35.32, 39.96, and 36.75 ppm. The effects of oxidant stoichiometric ratio on gas component volume percentages were also investigated at 550 °C, 25 MPa, 3% feed concentration, and 30 s residence time. As shown in , the volume percentages of CH_4, H_2, and CO decreased gradually with increasing oxidant stoichiometric ratio, becoming undetectable at 150% oxidant stoichiometric ratio, while CO_2 volume percentage increased steadily. This trend mirrors the behavior observed for TBP described in Section III.A.5.

IV. Conclusion

This work investigated the SCWO behavior of TBP and spent extraction solvent simulants, examining the influence of various reaction parameters on TOC removal and gas products. Comprehensive analysis of these factors led to the identification of optimal conditions for treating spent extraction solvent simulants: reaction temperature of 550 °C, pressure of 25 MPa, oxidant stoichiometric ratio of 150%, feed concentration of 3%, and residence time of 30 s. Under these optimal conditions, TOC removal exceeded 99.7% for spent extraction solvent simulants, with no detectable CH_4, H_2, or CO. Oxidant stoichiometric ratio and temperature were found to play important roles in controlling CH_4, H_2, and CO yields during decomposition of spent extraction solvent simulants. Residence time exhibited significant impact up to a threshold of 30 s, beyond which the effect diminished. Initial feed concentration had only slight influence on TOC removal. This research provides a foundation for future SCWO investigations on actual radioactive wastes.

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