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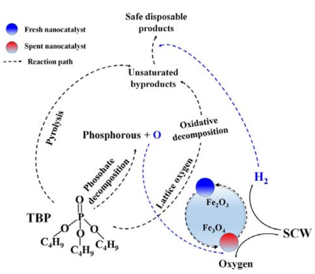
Decomposition of tributhyl phosphate at supercritical water oxidation conditions: Non-catalytic, catalytic, and kinetic reaction studies

Mohammadreza Kosari[a], Morteza Golmohammadi[b,c], Jafar Towfighi[b], Seyed Javad Ahmadi[d,*]

[a] Department of Energy Engineering, Sharif University of Technology, Azadi Avenue, Tehran, Iran
[b] Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
[c] Department of Chemical Engineering, Birjand University of Technology, P.O. Box 97175/569-212, Birjand, Iran
[d] Nuclear Science and Technology Research Institute, End of North Karegar Ave., Tehran, Iran

GRAPHICAL ABSTRACT



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ABSTRACT

Tributhyl phosphate (TBP) decomposition in supercritical water oxidation (SCWO) was performed with and without catalyst, at different temperatures ranging from 370 to 480 °C, and different reaction times. Ag_2O, CuO, Fe_2O_3, MgO, and ZnO synthesized by supercritical water were examined in TBP decomposition as the catalyst. TBP structure decomposed under the non-catalytic reaction; nevertheless, the results indicated that the use of catalysts improved the reaction efficiency, which calculated based on total organic carbon (TOC) removal, by far. However, TOC removal using Fe_2O_3 was 20% higher than the non-catalytic reaction. Having the ability in completion of the redox cycle, iron oxide catalytic nanoparticles preserve their stability and performance when used in a sequential TBP decomposition experiment. As for the estimation of the reaction rates, the kinetic constants were evaluated. Possessing a high predictive power with the accuracy more than 90%, the proposed kinetic equations can be applicable for further studies dealing with the TBP decomposition adopting SCWO.

1. Introduction

Water in its critical condition (T = 374 °C, P = 22.1 MPa) and even upper (i.e. supercritical region), namely SC-H_2O, is a distinct, inexpensive, and suitable medium for carrying out a wider range of chemical reactions, especially hydrothermal cracking, oxidation, gasification, decomposition, and extraction [1–5]. Many researchers have found it beneficial enough and a useful asset for the conversion of heavy hydrocarbons with high boiling point and low octane number to the lighter ones with low boiling point and high octane number [6–10]. As for the environmental usages, the prominent role of SC-H_2O has been universally understood so far. Being a benign and environmentally friendly medium without any organic and hazardous solvents, SC-H_2O is a completely applicable candidate to the applications demanding the high level of environmental protection.

Dielectric constant (ε) of SC-H_2O is much lower than that of H_2O in

* Corresponding author.
E-mail address: sjahmadi@aeoi.org.ir (S.J. Ahmadi).

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the standard condition (i.e. water @ T = 25 °C, P = 1 atm), strengthening SC-H_2O to solve the organic compounds and permanent gases such as oxygen. Above the critical point of water, its density varies between that of water vapor and liquid states under standard conditions, and actually its value is lower for SC-H_2O than for water. As the two former parameters, the ionic product of water declines drastically as water is heated to high-temperature zone [11]. All these changes make SC-H_2O distinguished from the polar medium possessing the gas-like diffusion rates and the high liquid-like collision rates, which are the two essential characteristics of a homogeneously oxidative environment without any mass-transfer resistance [12]. Taking advantage of these characteristics, supercritical water oxidation (SCWO) has been proposed as a promising method for the oxidative decomposition of hazardous organic materials containing heteroatoms such as sulfur, chlorine, phosphorous and nitrogen, which also could convert them into completely safe products (i.e. H_2O, CO_2, N_2, P, NaCl, etc.) [13–15]. Additionally, having minimized the mass-transfer limitations, we can trigger the SCWO to exhibit high reaction rate along with a short residence time and high conversion rate close to the unit.

Tributhyl phosphate (TBP) is an organophosphorus compound with a wide gamut industrial applications in the form of a complexing agent, solvent, herbicide, fungicide, defoamer, plasticizer etc. [16]. TBP is highly dangerous for the environment and biosystems because it is non-biodegradable and can gather up in sediments, soil and water, causing severe environmental pollution. Even the presence of a low TBP concentration of 4.2–18 mg l^{-1} could be toxic enough to hazard freshwater and living organisms. To name some toxical hazards of TBP on humans, high capacity for skin penetration, irritant effect on the skin and mucous membranes, and inhibition in human plasma cholinesterase should be taken into consideration [16].

The contaminated organic and inorganic compounds could be decomposed by means of thermal oxidation, catalytic oxidation [17], photocatalytic oxidation [18,19], and SCWO [15,20,21] etc. However, the low efficiency and production of the unwanted by-products (i.e. SO_x, NO_x) in thermal oxidation, demand pretreatment processes before catalytic oxidation, moreover, the limitation of useful photocatalysts can be measured as each method's shortcoming. SCWO can oxidatively decompose the organic and inorganic compounds and wastewater with high reaction rate, high miscibility rate of organic substances, high destructive yield, in very short residence time, without producing SO_x, NO_x. On the other hand, many researchers have paid attention to coupling supercritical water with the heterogeneous catalysts to increase the viability of SCWO for environmental purposes [22–26]. According to the reports, the use of the catalysts in SCWO increases the efficiency of the process in which the catalyst presence favors an increase in the oxidation rate, reduces the residence time and high temperature requirement, and possibly provides a better selectivity for competing reaction pathways [27].

Nanoscale catalysts provide a large surface area that is supposed to pave the way for an appropriate activity for a wide variety of reactions. For synthesizing super-fine and nanometric catalysts, numerous methods have been developed [28–32], among them SC-H_2O has been successful in producing a wide range of metal oxides with desirable features including smaller size, uniform shape, and large surface area.

To the best of our knowledge, the number of reports on catalytic oxidation of TBP using the catalytic nanoparticles is quite rare. Ambashta et al. worked on TBP decomposition in the presence of iron and iron-nickel nanopowders under a stationary magnetic field [33]. Due to the limited scientific reports on catalytic oxidation of TBP, in order to find the appropriate heterogeneous catalysts, those reports on decomposition and oxidation of the phosphoric organic compounds were checked. Sarkouhi et al. reported the decomposition of two different pesticides containing phosphorous in the presence of different metal nitrate salts including Hg, Cu, Cd, Ni, Pb, and Ag [34]. Another report shows using the metal oxide catalysts such as Fe_2O_3, WO_3, ZnO, TiO_2, CaO, FeO, Al_2O_3, MgO in the decomposition of the chemical weapons consisting of the phosphoric organic compounds [35].

Kinetics study of the chemical reaction plays an indispensable role in the simulation and scale-up procedures. As for the simulation of various hydrothermal reactions, in which hydrocarbons consist of a large proportion of initial feed, the two assets, viz. total organic carbon (TOC) and chemical oxygen demand (COD) have been appealing to many researchers [36–38] as the effective factors. These two factors have been known as the standardized and global parameters that are very useful and more controllable from both an environmental and scaling-up design standpoints. Lei et al. utilized the wet air oxidation method for the effluent treatment of a textile industry [36]. By the evaluation of TOC and COD variations versus time, they proposed a first-order kinetic model for the reaction. Another research by Sánchez-Oneto et al. reported that the two effluents of metal industry were treated in a continuous plug-flow reactor and the kinetic results for the oxidative reaction of both effluents were determined [39]. They exploited TOC and COD for kinetics studies and their proposed reactions were in close agreement with the first-order kinetic reaction. However, the kinetics of one of the effluents consisted of two steps: a fast step at the early time of reaction where TOC and COD variations were intense and a slow step in which TOC and COD changing profile had a very small decreasing slope versus time. In another research carried out by Abelleira et al. on the oxidation of isopropanol as a co-fuel in a continuous SC-H_2O reactor, a two-step first order kinetic model was applied to the SCWO process based on TOC and COD variation versus time, which means that the SCWO reaction took place in two well-separated steps: (i) a fast primary reaction, and (ii) a slow sequential reaction [37]. In continuation of Sánchez-Oneto et al. work, Vadillo et al. put forward an experiment to determine the performance of semi-industrial scale for oxidation of one of the effluents used by Sánchez-Oneto et al. [40]. They simultaneously followed thermal modeling along with kinetics simulation in terms of COD variation profile, which resulted in a two-step kinetic model including a fast-pace and a slow-pace step in the reaction. Thus, according to these aforesaid researches, one can infer that the first-order kinetic model satisfactorily expresses the involved reaction. The other works dedicated to the kinetic studies of organic solvent oxidation in SC-H_2O exploiting different feed-stocks such as EtOH and MeOH have also reported the validity of the applied first order kinetic model [41–45].

Herein, decomposition of TBP was investigated in SC-H_2O at different temperatures ranging from 370 to 480 °C, both in non-catalytic and catalytic reactions. Different nanoparticles, namely Ag_2O, CuO, Fe_2O_3, MgO, and ZnO synthesized by SC-H_2O were examined in catalytic TBP oxidative decomposition. The decomposition efficiency of the reactions was determined by measuring TOC parameter at the beginning and end of the reaction. Finally, the reaction rate was evaluated and proper kinetics equations for both non-catalytic and catalytic reactions were proposed.

2. Experimental

2.1. Materials

Tributhyl phosphate (TBP) used in this study as an initial feedstock and whose decomposition was evaluated in SCWO condition was of high purity, commercial grade with 99% assay, and was purchased from Merck. Hydrogen peroxide (H_2O_2) 30 wt% was also applied as an oxidant. The amount of H_2O_2 utilized in the experiment equaled twice its stoichiometry quantity. Silver nitrate, copper (II) nitrate trihydrate, manganese (II) nitrate tetrahydrate, zinc (II) nitrate hexahydrate, and iron (II) nitrate nonahydrate were of high purity commercial grade with 99.0%, 99.5%, 98.5%, 98.5%, 99.0% initial assay, respectively, used as precursors for the catalyst synthesis in supercritical water were also purchased from Merck.