



Review

Near and supercritical water. Part II: Oxidative processes

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ABSTRACT

This paper is a review of applications of near and supercritical water with a focus on supercritical water oxidation (SCWO). Hydrolytic and hydrothermal reactions have been reviewed in Part I [G. Brunner, Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes, J. Supercrit. Fluids, this issue]. The potential lies in the complete destruction of persistent, anthropogenic waste material. The obstacles in the technical application are due to the highly corrosive reaction medium and the precipitation of salts. Reactor construction is the decisive feature for a commercial process. First, tank type reactors had been favored. Corrosion was kept low by ceramic material and salt deposition was avoided by a stream of cold and clean water at the reactor vessel walls. Later, tubular reactor design was preferred, and several means to prevent corrosion and salt deposits have been applied.

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1. Introduction

This paper is a continuation of our review of the current state of near and supercritical water-based processes. Part I focuses on the hydrolytic and hydrothermal reactions. In this second part of the review, we focus on supercritical water oxidation (SCWO). As in Part I, the review is mostly based on research results that have been published in the Journal of Supercritical Fluids.

The review is based on the publications in The Journal of Supercritical Fluids, which give an excellent overview on the state of the art and the trends of development. The review is not a critical issue on all the published papers in the field. Neither time nor space allows doing this. Yet it was made sure that all the research groups contributing in the last few years, and before, were considered with their contributions. Nevertheless, there may some important contributions be missing, which is the fault of the author, without any intention.

The potential of SCWO lies in the complete destruction of persistent, anthropogenic waste material. The obstacles in the technical application are due to the highly corrosive reaction medium and

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the precipitation of salts. In the following, oxidative reactions are reviewed first, then reactor concepts, salt precipitation, and corrosion. Destruction of waste with supercritical water can be carried out over a wide range of temperatures, about 400–650 °C, at supercritical pressures. Dependence of the reactions on temperature is therefore important. The oxidation reactions in water are exothermic reactions ($\Delta h < 0$). Reaction equilibrium is shifted to educt compounds with increasing temperature. Yet for the oxidation reactions and temperatures involved in waste destruction, educt compounds are practically nonexistent at equilibrium. Reactions proceed under an increasing number of moles. High pressures, necessary for maintaining the supercritical environment, therefore favor educt compounds. Since reactions proceed in a dilute aqueous system, influence of pressure is not dominating reaction equilibrium. On the other hand, influence of temperature on reaction rate is important. According to experimental data, reaction rate can be enhanced, so that yield is raised by a factor of 10 by increasing the temperature by 100 K. Destruction of chemical compounds can be modelled globally by a first-order reaction, by which experimental data can be represented sufficiently well.

2. General aspects

One important aspect of SCWO is energy supply to maintain the reaction. Conditions for SCWO under energetically self-sufficient operation have been explored by Cocero et al. [2]. An empirical correlation for the calculation of reaction heat is proposed, in terms of C, H and O content in the waste. Minimum heating value required in the feed stream for energy self-sufficient operation is 930 kJ/kg. This value is equivalent, for instance, to a water stream containing 2% (w/w) *n*-hexane. Results have been verified in a pilot plant. Non-stationary phenomena have been modelled by Dutournié, and Mercadier [3]. They developed a simulation tool for non-stationary conditions at which irreversible damages to the reactor materials could occur. Oxygen supply is of no technical problem for larger installations. At the laboratory, oxygen may be problematic. An alternative method with oxygen supply by means of electrolysis has been proposed by Misch et al. [4].

3. Special substances

3.1. Methane

Quite a number of publications deal with the oxidation of methane. Dixon and Abraham [5] carried out catalytic partial oxidation over Cr_2O_3 . The presence of water in high concentration inhibited the methane conversion but promoted the yield of methanol. Increasing oxygen concentration dramatically reduced the yield of methanol. Diffusion flames in supercritical water with methane and methanol, first demonstrated by EU. Franck, were investigated by Steeper et al. [6]. The flames ignite at methane or methanol concentrations as low as 6 mol% at temperatures near 500 °C. The ignition-threshold concentrations rise as temperature is decreased to 400 °C. Kinetics and mechanism of methane oxidation in supercritical water have been reported by Savage et al. [7]. Methane conversions in supercritical water at 25.0 MPa and 525–587 °C ranged from 3 to 70%. The experimental results were used for a detailed chemical kinetics model, which is based on gas-phase oxidation mechanisms and kinetics and comprised 150 elementary reaction steps. Predicted activation energy for the pseudo-first-order rate constants of 36 ± 3 kcal/mol is similar to the experimental value of 44 ± 6 kcal/mol. Later, Savage et al. [8] published oxidation kinetics for methane/methanol mixtures in supercritical water. The presence of methanol accelerated the

rate of methane disappearance at 540 °C and 27.3 MPa. Presence of methanol led to higher methane conversions. Methane conversions at a residence time of 1.3–1.4 s were 8, 40, and 50% when the methanol concentrations were roughly 0, 5, and 13 times that of the methane concentration in the feed. The authors claim that gas-phase combustion chemistry and kinetics can be adapted to develop reliable detailed chemical kinetics models for SCWO. The density effect on partial oxidation of methane in supercritical water was analyzed by Sato et al. [9] in supercritical water at O_2/CH_4 ratios of 0.03 at 400 °C with a flow-type reactor. With increasing water density, methane conversion increased due to the formation of formaldehyde.

3.2. Methanol

A review of kinetic data for the oxidation of methanol in supercritical water was published by Vogel et al. [10]. Variations between the results from the different research groups were found to be due in part to differences in feed preheating and mixing, and residual oxygen dissolved in the organic/water feed stream. High initial feed concentrations yield higher apparent first-order rate constants, by producing hot zones in the reactor and also by decreasing the induction time. Experimental data can be affected by reactor wall catalysis. Consistent apparent first-order kinetics for the post-induction period were derived but recommendation on kinetic data for methanol SCWO could not be made because of limited information on induction time and insufficient knowledge on the influence of wall catalysis. Simple power law rate expressions are not adequate to describe the complex nature of autocatalytic oxidations over the full range of temperatures, feed concentrations, and residence times studied, but can be successfully applied to data sets obtained at similar experimental conditions. Catalysis of nickel metal during methanol gasification in supercritical water was investigated by DiLeo and Savage [11] at 500–550 °C. Without nickel, conversions up to 20% were reached after 2 h, in the presence of a Ni wire conversions of up to 90% were reached in less than 5 min. Hydrogen, carbon monoxide and carbon dioxide were the major products detected. With multiple uses, the Ni wire showed deactivation. Reaction kinetics of methanol and ethanol oxidation in supercritical water were investigated at 520–530 °C and 24.7 MPa by Hayashi et al. [12]. For methanol, conversion decreased with increasing initial methanol concentration a low concentrations (from 6.48×10^{-6} to 3.94×10^{-5} mol/l), conversion increased for high initial concentrations (from 2.23×10^{-4} to 1.55×10^{-3} mol/l). In the binary system, methanol conversion was accelerated by ethanol addition, whereas ethanol oxidation was slightly retarded by the presence of methanol. Oxidation of methanol with multiple injection of oxygen was carried out by Portella et al. [13]. This study also validated software (PROSIM) for the scale-up of industrial units, to minimize the amount of energy supplied to the system and to optimize the energy generated by the oxidation of organic wastes.

3.3. Ethanol

The oxidation of ethanol in subcritical water was studied by Hirotsuka et al. [14] at temperatures between 170 and 230 °C, a fixed pressure of 23.5 MPa, residence times from 180 to 580 s, initial concentration of ethanol 25 mmol/l and of oxygen from 50 to 150 mmol/l. The reaction orders are 0.86 for ethanol and 1.15 for oxygen.

3.4. Propane

Armbruster et al. [15] investigated the partial oxidation of propane in sub- and supercritical water to oxygen-functionalized

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