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Kinetics of supercritical water oxidation of isopropanol as an auxiliary fuel and co-fuel

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HIGHLIGHTS

- Isopropanol is a suitable fuel for SCWO and is resistant to pyrolysis–hydrolysis.
- Kinetic model of IPA as auxiliary fuel in SCWO start-up stage was proposed.
- Kinetic model of IPA as co-fuel in SCWO under steady-state was proposed.

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ABSTRACT

Nowadays the studies that deal with the supercritical water oxidation (SCWO) of problematic wastes are focused in the search of practical solutions for the SCWO main drawbacks: corrosion, plugging, and high running costs. Regarding the high running costs, an important fact is that significant energetic requirement does exist during the process start-up, as well as to reach an autothermal operation if the waste to be treated does not have enough inherent heating value. The use of organic solvents [such as methanol (MeOH), ethanol (EtOH) or isopropanol (IPA)] as auxiliary fuel (to aid running the start-up stage)/co-fuel (to improve the steady-state stage) in the SCWO of certain wastes is emerging as a possible solution to help overcoming these problems. Many works in the literature use IPA as fuel in the SCWO process. However, there are very few laboratory studies that detail, from a practical point of view, the kinetics of the IPA oxidation in supercritical water (SCW) with the aim of unveiling the insights of its behaviour as an auxiliary fuel/co-fuel in the SCWO process and the development of further works on the simulation at a larger scale.

The aim of this work was to develop a detailed and practical set of kinetic equations easily applicable to further studies on simulation and experimentation at a larger scale. In addition, pyrolysis–hydrolysis tests in SCW were also conducted concluding that, in the case of IPA, these reactions do not significantly interfere with SCWO. The required experimentation was performed in a tubular reactor system at laboratory scale at a constant pressure of 25 MPa, using pure oxygen as oxidant and monitoring the efficiency of the oxidation process in terms of reduction in chemical oxygen demand (COD) and total organic carbon (TOC) versus the residence time. This study consists of two major blocks: (a) a set of experiments on SCWO of IPA under a constant excess of oxygen (=100%) and different temperatures ranging from 673 to 773 K. Two-parameter mathematical models involving two steps (a fast reaction followed by a slow reaction) were proposed to describe the IPA SCWO kinetics and to calculate the corresponding kinetic parameters, assuming a zero order for oxygen concentration; and (b) a complementary set of experiments on SCWO of IPA at a constant temperature (748 K) and different oxidant coefficients from $n = 0.5$ (50% of stoichiometric oxygen) to $n = 2.0$ (100% oxygen excess), proposing a kinetic model for oxygen concentration dependence whose parameters were determined using a Runge–Kutta-fourth-order algorithm. The kinetic models proposed allow the prediction of the COD or TOC conversion with or without respect to oxygen supply in order to optimize the SCWO operating conditions and to minimize investment and operating costs.

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1. Introduction

1.1. Generalities on SCWO of wastes

Supercritical Water Oxidation (SCWO) is a high-pressure high-temperature process for the efficient destruction of an extensive diversity of aqueous organic wastes [1] such as textile wastewater, wastewater from terephthalic acids, food waste, municipal excess sludge, manure sludge, oily wastes, alcohol distillery wastewater, obsolete chemical weapons, wastes from nuclear industry or pharmaceutical and biopharmaceutical wastes [2,3]. SCWO is based on the oxidation in aqueous medium under conditions over the critical point of pure water, usually in the range [673,923] K and commonly at a pressure around 25 MPa. Under these conditions, water exhibits unique physical–chemical properties that make it an effective medium for oxidation, where organics and oxygen form a homogeneous phase. Thus, mass transport limitations are minimized leading to high reaction rates and conversions close to unity in short residence times and small reactor volumes. Moreover, as the oxidation reactions are exothermic, autothermal operation and even heat production could be achieved in the SCWO process [4–7].

As an example of the latest trends in this field, the implementation of the SCWO process as tertiary treatment in the sludge line of wastewater treatment plants (WWTPs) is increasingly regarded as an alternative to incineration [8–10], in order to promote the removal of the excess sewage sludge [3,10–14]. The studies focused on the improvement of sewage sludge SCWO performance, effectiveness and reliability are quite numerous [3,15]. In fact, the main drawbacks that keep SCWO away from being massively implemented on a full-scale at WWTPs and other industries are corrosion, plugging and high running costs [3]. In particular, severe operating conditions (high temperature, high pressure, high concentration of oxidant and extreme pH value) together with high concentration of ionic species, free radicals, acids and inorganic salts result in severe corrosion problems in the SCWO reactor and the inlet/outlet pipelines.

To help overcoming these limitations, accomplish an autothermal operation and, in general, a better performance of the SCWO process, methanol (MeOH), ethanol (EtOH) or isopropanol (IPA) can be added as auxiliary fuels during the start-up or as co-fuels during the steady-state of the SCWO process for certain wastes. Some major candidates among the wastes that may require the use of a fuel are obsolete chemical weapons, biomass slurries, sewage sludge, manure sludge or, in general, wastes with low inherent heating value, high acute toxicity and/or high concentration of ammonia [16,17].

1.2. Auxiliary fuels for SCWO

It is well known that the energy consumption to heat the waste externally during the SCWO process may become prohibitive upon scale-up from a laboratory system [3]. In addition, an excessive preheating during the process start-up to initiate rapid reaction effectively, limits the concentration of waste that can be processed due to char formation and plugging [18] in the preheating pipeline, mainly in the case of high salt-containing wastes. Furthermore, in the case of wastes containing solids (e.g., biomass slurries) it is necessary to work at high flow rates to avoid solids deposition, so the start-up of the process would require too much energy. In this way, it is better to start-up the process at a low flow rate and, afterwards, to increase the flow rate gradually. This is why the use of an auxiliary fuel to carry out the SCWO start-up becomes mandatory, allowing the heating process to start at a low flow rate, and once the required temperature is attained, to proceed to gradually increase the system flow rate. Then, after the steady-state is reached (under the desired operating conditions), it is time to proceed with the injection of the waste.

As a result, the use of an auxiliary fuel such as IPA [that is easily oxidized by SCWO and presents a higher heat of reaction ($\Delta H_r = -1908$ kJ/mol) than MeOH ($\Delta H_r = -650$ kJ/mol) and EtOH ($\Delta H_r = -1279$ kJ/mol)]* to conduct the start-up of the SCWO process, induces a proper operation in this early stage and greatly facilitates reaching the subsequent steady-state stage efficiently. The employment of IPA to start-up the SCWO process is intended to maximize the heat of reaction generation, in order to minimize the time to reach the suitable operating conditions (autothermal operation) before the considered waste is injected and subjected to SCWO under steady-state. During the SCWO start-up performed using an organic solvent, it is also favourable not to restrict the addition of oxidant (air or oxygen in excess) to aid the maximization of the heat of reaction generation and the minimization of the start-up operating time. Besides, this does not entail an excessive increase of the overall operation costs, as it only constitutes a punctual overspending during the start-up of the process that, moreover, is offset enough and to be spared by the patent reduction in the start-up operation time. (*Heat of reaction values estimated at 673 K and 25 MPa according with the empirical equation proposed by Cocero et al. [4]).

The application of a two-step first order kinetic model to the SCWO process assumes that the SCWO reaction occurs in two well differentiated phases: (1) a fast initial reaction in which easy oxidizable molecules are decomposed at a high rate to CO_2, H_2O and a mixture of intermediate products of a more refractory nature, followed by (2) a slow subsequent reaction where the main part of those intermediates formed before and other refractory molecules initially present in the wastewater/waste, are progressively decomposed to more simple molecules (alcohols, organic acids, etc.) and mineralized down to CO_2, H_2O, N_2, and salts. It is important to point out that depending on the operation temperature, there are some refractory intermediates (such us acetic acid and ammonia) that may remain in the effluent even at the higher residence times studied. This type of kinetic model was satisfactorily applied in our previous works dealing with the oxidation of cutting fluids in SCW on laboratory scale [19] and pilot plant scale [20]. Two-step first-order kinetics has also been proposed previously in the literature for other feeds such as wastewater from the textile industry, oxalic acid and acrylic acid [21,22].

This work, which aims to describe the kinetics of the SCWO process start-up using IPA, proposes and develops a two-step first-order kinetic model according to the results obtained from SCWO of IPA experiments at constant pressure and oxidant excess conditions, and under different temperatures and residence times. The corresponding section of this work (Section 3.2) includes two kinetic models of this nature, each of them based on the chemical oxygen demand (COD) removal and total organic carbon (TOC) removal results, respectively. This approach will be useful for further works on IPA as auxiliary fuel in the start-up stage of the SCWO process on larger scales, in order to aid running this stage while minimizing the required external preheating electrical power.

1.3. Co-fuels for SCWO

After reaching the proper steady-state conditions for the SCWO of certain waste, the oxidant consumption becomes an important factor to consider in the economic balance of the process [15]. Therefore, the oxidant coefficient must be optimized to minimize running costs without impairing the organic matter removal during the SCWO process. Besides, the addition of moderate doses of an organic solvent (e.g. IPA) as co-fuel in the SCWO of wastes under steady-state conditions facilitates the maintenance of an