Supercritical Water Oxidation of Isopropanol under Conditions of both Oxidant Deficit and Excess

Jose Abelleira*, Jezabel Sánchez-Oneto, Juan R. Portela, Enrique Martínez de la Ossa

University of Cádiz, Faculty of Sciences, Department of Chemical Engineering and Food Technologies
Campus Universitario Río San Pedro, 11510 Puerto Real (Cádiz), Spain,
jose.abelleira@uca.es

Treatment of a wide variety of aqueous organic wastes by means of supercritical water oxidation (SCWO), [T > 374 °C and P > 220 bar], is well known to be very effective. However, in some cases (e.g. biomass slurries, obsolete chemical weapons, etc.) the addition of an auxiliary fuel such as methanol (MetOH), ethanol (EtOH) or isopropanol (IPA) is beneficial to overcome certain SCWO limitations and to accomplish an autothermal operation.
The main objective of this work is to implement a set of laboratory tests, at different temperatures (T), oxidant coefficient values ($n = oxygen_{supplied} / oxygen_{stoichiometric}$) and residence times ($t$), needed to know the behavior of IPA in the SCWO process and its suitability as a make-up fuel in comparison to EtOH and MetOH.
All assays were carried out in a continuous flow reactor system, at a constant pressure of 250 bar and temperatures ranged from 400 °C to 500 °C. The amount of oxygen supplied ranged from total defect (pyrolysis) to oxygen excess. The concentration of make-up fuel was settled around 10 g/l at the reactor entrance. Results obtained from pyrolysis experiments show that this reaction can not be neglected, since up to 11.68 % of the total chemical oxygen demand (TCOD) removal was attained at 500 °C. Operating with oxygen excess ($n = 2$), TCOD removal is clearly enhanced by the temperature from 38 % at 400 °C to > 99 % at 500 °C. Results in terms of total organic carbon (TOC) removal are in accordance with TCOD removal. Considering $T = 460$ °C and $t \approx 12 - 40$ s, results of this work show that the highest level of TCOD removal is attained for SCWO of EtOH, followed by MetOH and then, by IPA.

1. Introduction

Supercritical Water Oxidation (SCWO) is a high-pressure high-temperature process for the efficient destruction of a wide variety of aqueous organic wastes (Portela et al., 2009). SCWO basically consists on the oxidation in aqueous medium under conditions over the critical point of pure water, usually in the range 400–650 °C and at a pressure of 250 bar. At these conditions, water exhibits unique physical-chemical properties that make it an effective reaction medium for oxidation, 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, an autogenic operation and even the heat production could be achieved in the SCWO process. Nevertheless, the energy

consumption of heating the waste externally becomes prohibitive upon scale-up from a laboratory system. In addition, excessive preheating to initiate rapid reaction effectively limits the concentration of the waste that can be processed, due to char formation and plugging. To aid the overcoming of these limitations and the accomplishment of an autothermal operation, an auxiliary fuel [e.g. methanol (MetOH), ethanol (EtOH) or isopropanol (IPA)] can be added during the start-up and/or steady state of the SCWO process for certain wastes. Primary candidates could be obsolete chemical weapons, biomass slurries such as sewage sludge and manure sludge or, in general, wastes with low inherent heating values and high acute toxicity.

Several researchers have used auxiliary fuels in SCWO (Marrone et al., 2005), and basic kinetics equations can be found in the literature (Hunter et al., 1996; Anitescu et al., 1999; Rice and Croiset, 2001; Schanzenbächer et al., 2002). However, as far as authors are concerned, in the case of IPA none of those studies presented an exhaustive kinetic analysis including the oxygen concentration dependence.

For that reason a set of laboratory tests have been performed at different temperatures (T), oxidant coefficient values (n) and residence times (t), with the aim of getting to know the behavior of IPA in the SCWO process and its suitability as an auxiliary fuel in comparison to EtOH and MetOH. It is also important to carry out control pyrolysis tests, at comparable conditions to those employed in the SCWO experimentation, in order to determine its relevance on final results (Anitescu et al., 1999).

2. Material and Methods

SCWO experiments were carried out in a continuous flow reactor system used by the authors in several previous studies (Sánchez-Oneto et al., 2007; Portela et al., 2009). The organic and oxidant feed streams were pressurized in two different lines by high-pressure metering pumps and then preheated separately. Croiset et al. (1997) evidenced that H_2O_2 completely decomposed in the preheaters. After preheating, the two lines were mixed at the reactor entrance.

Upon exiting the reactor, the effluent was rapidly cooled in a counter current heat exchanger and afterwards, the system pressure was reduced by using a back-pressure regulator valve. The product stream was then separated into liquid and vapour phases.

Total chemical oxygen demand (TCOD) and total organic carbon (TOC) contents of the liquids samples were monitored. All analyses were performed according to the standard method for water and wastewater analysis (APHA, 1998). Gas samples were analyzed by gas chromatography using a Thermal Conductivity Detector (TCD).

3. Results and Discussion

3.1 SCWO of IPA under conditions of oxidant excess

Percentages of both TCOD and TOC removal in the SCWO experiments of IPA solutions are shown in Figure 1. All the assays were carried out using an oxygen concentration above the stoichiometric value (oxidant coefficient n higher than 1.5; $n = oxygen_{supplied}/oxygen_{stoichiometric}$), so no oxidant limitation occurred. Only at the lowest temperature (400 °C), a few differences were found between the TCOD removal

and the corresponding TOC removal at the same experimental conditions. This means that both parameters could be used to predict the reaction conversion.

At 500 °C, which is a usual temperature in SCWO at industrial scale, a conversion close to unity (99.5 %) is achieved for a residence time of 8 seconds. However, conversion is lower than 60% at 400 °C, even in 60 seconds (an elevated residence time for SCWO). As expected, the temperature of the reaction is a relevant operating variable: the higher the operation temperature the higher the organic matter removal.
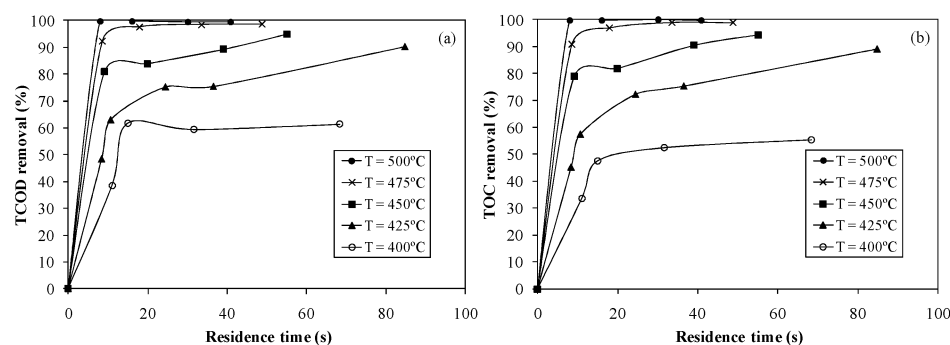

Figure 1: Experimental data for (a) TCOD removal and (b) TOC removal in SCWO experiments of IPA solutions. [P = 250 bar, T = 400 °C – 500 °C, n > 1.5].

Pseudo-first kinetic model was tested over the experimental data shown in Figure 1, to obtain the corresponding kinetic equation and its dependency with the temperature, according to the Arrhenius law. However, no satisfactory result has been obtained with this simple model. The evolution of both TCOD and TOC removal with respect to residence time exhibit a fast reaction first stage, followed by a slow reaction second one. In order to represent this evolution satisfactorily, a two-step (fast and slow) first-order model is recommended and it will be proposed in a further study on its kinetics. In the literature, similar tendency can be found for the hydrothermal oxidation of other compounds or wastes, and two-step first-order kinetics has also been proposed for wastewater from the textile industry, cutting oils, oxalic acid and acrylic acid (Lei et al., 2000; Shende and Levec, 2000; Sánchez-Oneto et al., 2007).

3.2 SCWO of IPA under conditions of both oxidant deficit and excess

Figure 2 shows results in terms of TCOD and TOC removal (%), for a set of SCWO experiments of IPA solutions. The oxidant coefficient (n) ranged from 0.5 to 2.

The organic matter removal rate is enhanced with increasing oxidant coefficient. However, it has to be pointed out, that oxygen dependence is more patent below the stoichiometric value for oxygen concentration than above it. In fact, few differences occurred between the experimental data obtained for tests with n = 1.25 and n = 2. These statements entail the following consequences: on the one hand, it has been proved that raising n up to values around 2 is not necessary for achieving significant conversion rates; on the other hand, it is suitable and necessary to establish a kinetic analysis including the oxygen concentration dependence (Sánchez-Oneto et al., 2008). This
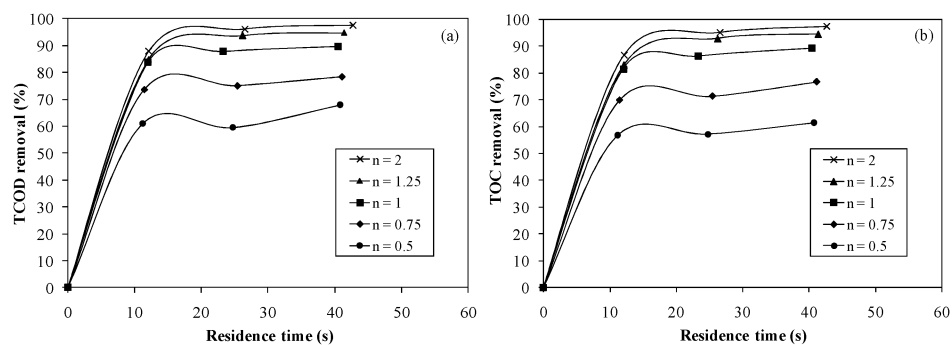
Figure 2: Experimental data for (a) TCOD removal and (b) TOC removal in SCWO experiments of IPA solutions. [P = 250 bar, T = 460 °C, n = 0.5 – 2].

would complete the works on kinetics for the SCWO of IPA, which can be found in the literature and where the oxygen concentration dependence is not taken into account (Hunter et al., 1996).

3.3 Percentage of TCOD removal due to pyrolysis during SCWO tests

References on pyrolysis of alcohols such as IPA, EtOH and MetOH can be found in the literature (Barnard, 1960; Trenwith, 1975; Anitescu et al., 1999). Nevertheless, as far as authors are concerned, few studies have recently been performed on alcohols pyrolysis related to the operation in continuous flow reactor systems.

IPA pyrolysis experiments were performed at 460 °C and 500 °C, with a constant operating pressure of 250 bar. For T = 460 °C, the operating residence time corresponded to the central value of the range used in the SCWO experimentation ($t \approx 25$ s). For T = 500 °C, the residence time was closer to the higher value ($t \approx 38$ s), in order to obtain pyrolysis results for the most severe conditions used in the SCWO experimentation conducted in this work. In this case, deoxygenated water was used to prepare IPA solutions. Obtained results showed that this reaction cannot be neglected at temperature ≥ 500 °C, since at least 11.63 % of TCOD removal was attained. However, for most of the experiments in this study, pyrolysis process can be neglected, since at a temperature ≤ 460 °C the TCOD removal values are below 3.65 %.

3.4 SCWO of IPA Vs. EtOH & MetOH

SCWO of isopropanol, ethanol and methanol has been carried out to assess their suitability as auxiliary fuels for SCWO. Figure 3 shows experimental results in terms of TCOD removal (%) of SCWO tests performed at P = 250 bar, T = 460 °C and n = 2.

Regarding the oxidation rate, EtOH would be the best auxiliary fuel since the highest TCOD removal (%) was obtained in its case (99.6 % at $t \approx 40$ s). A bit lower results have been obtained for SCWO of MetOH at $t \approx 40$ s (99.5 %). This difference is more patent at $t \approx 12$ s (99.4 % for EtOH vs. 98.2 % for MetOH). In this work, IPA is the most refracting fuel for the studied residence times. These results are partially in agreement with Bourhis et al. (1995) who mentioned that EtOH exhibits a higher reaction rate than IPA and MetOH (as in our work). However, these authors found that

IPA is more easily oxidized than MetOH (just the opposite in comparison to our experimental data). In Rice and Croiset (2001) it is again quoted that the conversion rate of EtOH is faster than those of MetOH and IPA. In fact, for the procedure operating conditions and references presented in Rice and Croiset (2001), EtOH appears to be 50% converted at 430 °C in 1.25 s, IPA requires 1.6 s to be 50% converted at 430 °C, and methanol requires more than 3.0 s for 50% conversion.
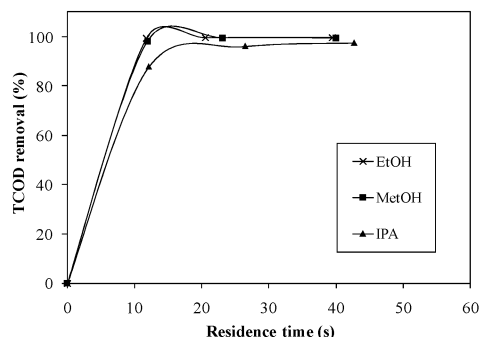

Figure 3: Experimental values for TCOD in SCWO experiments of IPA, EtOH and MetOH solutions. [P = 250 bar, T = 460 °C, n = 2].

4. Conclusion

SCWO of IPA solutions was performed in a continuous flow reactor system under temperatures from 400 °C to 500 °C, and a constant pressure of 250 bar. A conversion close to unity (TCOD removal and TOC removal > 99.5 %) is achieved in 8 seconds residence time, at $T = 500$ °C and $n = oxygen_{supplied} / oxygen_{stoichiometric} > 1.5$. The organic matter removal rate is significantly enhanced with increasing temperature and amount of oxygen (from $n = 0.5$ to $n = 1.25$). Results from pyrolysis tests show that this reaction cannot be neglected at a temperature ≥ 500 °C. SCWO experiments with auxiliary fuels show that the highest reaction rate was achieved in the case of EtOH, and the lowest in the case of IPA. However, since the IPA reaction enthalpy is significantly higher than in the case of EtOH or MetOH and the difference regarding the oxidation rate is not too high, further studies have to be conducted in the future in order to determine which of these auxiliary fuels could be the most suitable for the SCWO process at pilot plant and industrial scale. In this case, it must be taken into account other factors such as the initial temperature needed to start the oxidation reaction, the price of the auxiliary fuel and safety considerations.

Acknowledgements

References

American Public Health Association (APHA), 1998, Standard methods for the examination of water and wastewater, APHA, 20th ed. Washington D.C., USA.

Anitescu A., Zhang Z., and Tavlarides L.L., 1999, A kinetic study of methanol oxidation in supercritical water, Industrial & Engineering Chemistry Research 38, 2231-2237.

Barnard J.A., 1960, The pyrolysis of isopropanol, Transactions of the Faraday Society 56, 72-79, DOI: 10.1039/TF9605600072.

Bourhis A.L., Swallow K.C., Hong G.T., and Killilea W.R., 1995, The use of rate enhancers in supercritical water oxidation, Innovations in Supercritical Fluids 23, 338-347.

Croiset E., Rice S.F. and Hanush R.G., 1997, Hydrogen-peroxide decomposition in supercritical water, AIChE Journal 43, 2343-2352

Hunter T.B., Rice S.F. and Hanush R.G., 1996, Raman spectroscopic measurement of oxidation in supercritical water. 2. Conversion of isopropyl alcohol to acetone, Industrial & Engineering Chemistry Research 35, 3984-3990

Lei L., Hu X., Chen G., Porter J.F. and Yue L.P., 2000, Wet air oxidation of desizing wastewater from the textile industry, Industrial & Engineering Chemistry Research 39, 2896-2901.

Marrone P.A., Cantwell S.D. and Dalton D.W., 2005, SCWO system designs for waste treatment: application to chemical weapons destruction, Industrial & Engineering Chemistry Research 44, 9030-9039

Portela J.R., Sánchez-Oneto J., García-Jarana B., Nebot Sanz E. and Martínez de la Ossa E., 2009, Comparison of different hydrothermal processes for the elimination of cutting fluids wastes, Chemical Engineering Transactions, 17, 245-250

Rice S.F. and Croiset E., 2001, Oxidation of simple alcohols in supercritical water III. Formation of intermediates from ethanol, Industrial & Engineering Chemistry Research 40, 86-93

Sánchez-Oneto J., Portela J.R., Nebot E. and Martínez de la Ossa E., 2007, Hydrothermal oxidation: application to the treatment of different cutting fluid wastes, Journal of Hazardous Materials 144, 639-644.

Sánchez-Oneto J., Mancini F., Portela J.R., Nebot E., Cansell F. and Martínez de la Ossa E.J., 2008, Kinetic model for oxygen concentration dependence in the supercritical water oxidation of an industrial wastewater, Chemical Engineering Journal, 144, 361-367.

Schanzenbächer J., Taylor J.D. and Tester J.W., 2002, Ethanol oxidation and hydrolysis rates in supercritical water, Journal of Supercritical Fluids 22, 139-147

Shende R.V. and Levec J., 2000, Subcritical aqueous phase oxidation kinetics of acrylic, maleic, fumaric and muconic acids, Industrial & Engineering Chemistry Research 39, 40-47.

Trenwith A.B., 1975, Thermal decomposition of isopropanol, Journal of the Chemical Society, Faraday Transactions 1, 71, 2405-2412, DOI: 10.1039/F19757102405.