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Temperature control in a supercritical water oxidation reactor: Assessing strategies for highly concentrated wastewaters

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ABSTRACT

Supercritical Water Oxidation (SCWO) is a high temperature and pressure process whose operating conditions are beyond the critical point of pure water (Tc = 374 °C and Pc = 221 bar), and is a powerful technology to treat wastewaters in a clean and effective manner. Moreover, the heat released during the oxidation reaction allows the recovery of energy and improves the efficiency of the process. In those cases where the reaction of high concentrated wastewaters generates a high temperature profile in a thermally insulating tubular reactor, a temperature control system is necessary to keep the operation within safety limits. With the aim of controlling the temperature along the reactor, both cooling water and oxidant split injectors have been installed in a 25 kg/h pilot plant. Experimental tests have been carried out to compare the operation of the pilot plant before and after those two improvements. Intermittent water injections provide a quick and located cooling. Each injection reduces the temperature inside the reactor by around 20–40 °C, and the frequency between injections depends on the exothermicity of reactions. When oxidant split is added in two injections, air in defect for the first injection (n ≈0.5) and in excess for the second one (n ≈1.2), the peak of temperature can also be smoothened and the development of the reaction can be controlled. In both cases, the temperature profile along the reactor is effectively controlled and the reaction remains within safe limits that allow a stable and reliable treatment of highly concentrated wastewaters.

1. Introduction

Above the critical point (Tc = 374 °C and Pc = 221 bar), water exhibits interesting properties that allow the destruction of organic wastewaters by oxidation. Thanks to the homogeneity of the medium under these conditions, there is no mass transfer limitation and high reaction rates are reached to oxidize organic and inorganic compounds [1]. Moreover, residence time periods needed are shorter than 1 min and a high removal efficiency level is obtained, at the same time, non-harmful by-product are generated [2]. This allows the effective treatment of a wide variety of industrial waste [3–9]. Due to the extreme conditions required, SCWO is a costly process. On the other hand, the treatment of highly concentrated wastewaters may generate a large amount of energy and reduce operation costs considerably. Oxidation reactions are strongly exothermic and wastewaters with a high concentration (Chemical oxygen demand (COD) > 80 gO_2/l) may release enough heat and make their treatment by SCWO an attractive process for energy recovery. In a conventional SCWO plant, the wastewater feed and the oxidant are mixed at the tubular reactor entrance, so there is not a direct control of the energy released inside the reactor [10]. In a previous work [11], the possible energy recovery from a 1 m^3/h SCWO plant was studied and quantified. It showed that cutting oil wastewater with an initial COD concentration of 50 gO_2/l allowed the recovery of a maximum of 118 kW, e.i., 71% of the energy wastewater content. In those cases where highly concentrated wastewaters (COD concentrations > 50 gO2/l) are treated, the heat released by the reactions can be so high that it may be necessary to control the temperature reached. Since the temperature profile in the reactor may increase very quickly, the initial concentration of the wastewater to be treated is limited by the maximum temperature supported by the reactor material (stainless steel, Hastelloy, Inconel, etc). Vadillo et al. [12], described the thermal control of the SCWO process as one of the key points to improve this technology and to foster it for its commercial development [13]. In the case of high organic load and high reaction heat it is necessary to control the temperature along the reactor. It

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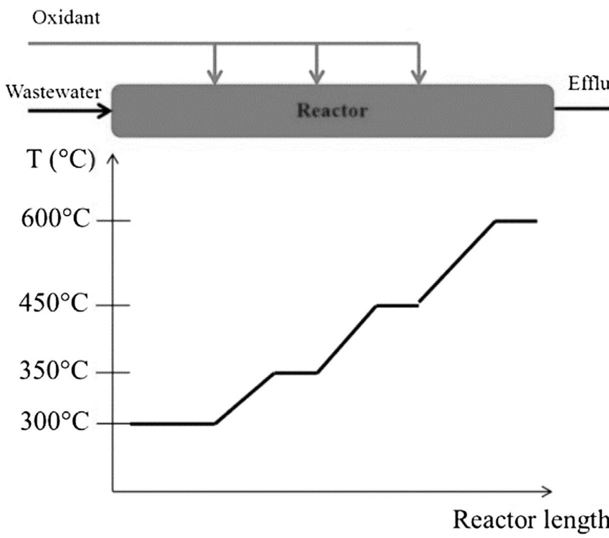

Fig. 1. Theoretical temperature profile in a HOO reactor [16].

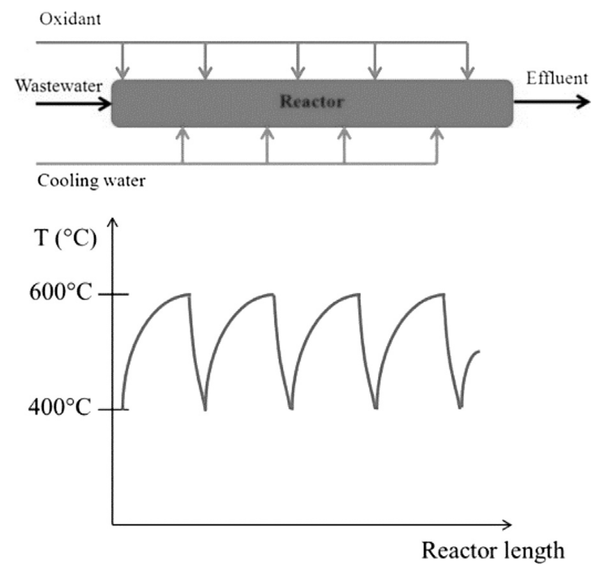

Fig. 2. Theoretical temperature profile in a Chematur type reactor [19].

should be maintained below the material safety limits, while the formation of hot spots as a consequence of extremely high release of heat at concrete zones of the reactor should be avoided [14]. As an example, the reactor of the pilot plant at University of Cádiz is made of ¾″ stainless steel 316L tubing with a special wall thickness of 3.365 mm to increase its pressure resistance. According to the data sheet supplied by the manufacturer, when operating at room temperature the service pressure is 465 bar. When the temperature increases, the pressure limit starts to decrease gradually, and the maximum allowed pressure is 352 bar at 537 °C. Beyond 537 °C, stainless steel resistance falls drastically, and the service pressure drops to only 80 bar when the operating temperature is 649 °C. According to this, the temperature to be reached throughout the reactor should be lower than 550 °C, this would ensure safe operation at a pressure of 250 bar.

For these reasons, to maintain safe conditions and carry out optimal energy recovery, SCWO plants fitted with a tubular reactor and treating highly concentrated wastewaters must have a very strict thermal control. This can be achieved by means of injections of cooling water and multioxidant at different points along the reactor [15]. The use of a direct injection of a cool water stream in a tubular reactor is an efficient way to rapidly decrease the temperature of a reactor zone and, therefore, to control the excess of temperature in the reaction medium. Furthermore, another way to control the excess of heat released during the reactions consists on properly distributing the oxidant along the reactor. For this purpose, two or more oxidant injections can be used to decrease the concentration of oxygen at the reactor entrance [16].

Several authors have developed and studied new configurations or strategies to improve the thermal control of the process in tubular reactors. Kim et al. [17] studied the SCWO of transformer oil contaminated with polychlorinated biphenyls (PCBs), and they simulated a SCWO reactor including cool water injection points to control the release of heat, maintaining an operating temperature between 500 and 600 °C. Cansell [18] patented a method to treat waste by hydrothermal oxidation, the so called "HOO" Reactor Concept consists of multioxidant injections at several points along the reactor, as can be seen in Fig. 1. The reaction starts at 300 °C to avoid the need of injecting large amounts of oxidant at the reactor entrance. The amount of pure oxygen injected at each point of the reactor is the quantity that is soluble in water at 250 bar and at the temperature of that point of the reactor, maintaining a monophasic reaction medium. This allows the control of the process and starting the reaction at 300 °C, which also enables the treatment of larger amounts of organic loads and to go over the critical point of water without an external supply of energy. Some oxidation tests were carried out using methanol in order to build and validate a simulation model before scaling-up the reactor to an industrial scale, using PROSIM software [14]. and a discrete model [19]. The numerical predictions between models and the actual experimental data matched closely in both cases. The reactor was also tested using olive oil mill wastewater as the feed. Temperature profiles generated were compared with those predicted by PROSIM [20].

Yu et al. [21] investigated the suitability of a catalytic SCWO reactor for the treatment of oily wastewater. They observed that when using Cu2+, Mn2+ and Co2+ as catalyst, the performance of the reactor improved and COD removals reached over 90%. Gidner & Stenmark [22] describe the "Chematur" Type Reactor, that allows the thermal control of the reactor associated to exothermal oxidation reactions. As can be seen in Fig. 2, multioxidant and cool water injections can be carried out to distribute the oxidant properly and to avoid hot spots along the reactor. The operating procedure of this kind of reactor consists on injecting a particular quantity of oxidant below the stoichiometric ratio at a temperature around 400 °C at the reactor inlet. Once the oxidant is completely consumed and the temperature has increased to around 600 °C, a cool water stream is injected to decrease the reaction medium temperature down to approximately 400 °C.

Then, a new oxidant injection is completed and temperature goes up to 600 °C. Thus, a new cool water injection is carried out to decrease the reaction medium temperature to 400 °C. This temperature regulation is repeated until the complete destruction of the organic matter in the wastewater. This type of reactor was developed and commercialized by "Chematur Engineering", a society that has developed industrial processes such as Aquacat and Aquacritox. The company SCFI Group Ltd. (SuperCritical Fluid International), located in Cork (Ireland), purchased Aquacritox technology. Since this technology has been developed by a private company, detailed scientific results are not available in the literature. Besides the reactor configuration cited above, Brunner [23] described other reactor construction features for commercial purposes.

In this work, both cooling water injections and split addition of air have been installed to control the temperature along the tubular reactor in a 25 kg/h pilot plant. Regarding the use of cooling water, both intermittent and continuous addition of cooling water have