Experimental Study of the Initiation of the SCWO Reaction Using Different Static Mixer Configurations

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The objective of this project is to experimentally study the initiation of the SCWO reaction of concentrated IPA solutions, by mixing a water + IPA stream and an air stream at different operational conditions (temperature, velocity). The reaction start was monitored experimentally measuring the temperature inside the mixer and by TOC determination in liquid samples. The experimental facility was modeled assuming plug and using different kinetic models. It was found that at temperatures lower than 450ºC depending on the mixer design the reaction proceeds slowly while when reaching higher temperature the raised sharply indicating a much faster reaction mechanism. The description of the phenomenon is similar with the described ignition of hydrothermal flames in literature. Almost complete TOC removals have been obtained in residence times lower than 1 s.

INTRODUCTION

Supercritical water oxidation (SCWO) technology presents important environmental advantages for the treatment of industrial wastes. Injection of the wastes at subcritical temperature has become an important aspect in the design of new SCWO reactors. The mixing of the oxidant and the waste aqueous stream previous to the reaction and the reaction initiation seems to be a key aspect when designing a new reactor. Despite its importance there is very little done in this subject.

In the ETH of Zurich the direct injection of the waste into a hydrothermal flame generated inside the reactor was developed as a solution to avoid the external preheating of the wastes up to supercritical conditions ([1], [2]). Hydrothermal flames were first described by Franck and coworkers [3, 4]. The presence of a flame in an SCWO system would be expected to enhance the destructive abilities of the SCW medium [5]. However, only a few works about hydrothermal flames have been published [5-7]. In general flames ignite spontaneously beyond a certain temperature normally between 400 and 500º C. In general ignition conditions of the flames depend on the fuel, the oxidant, the ratio fuel/oxidant and the geometry of the injection system.

The objective of this work was the study of the reaction initiation of the supercritical water oxidation reaction in a tubular mixer. For doing so the temperature profile inside the tubes as monitored.

EXPERIMENTAL

All the experiments were carried out in the pilot plant of the University of Valladolid. It has a maximum capacity of 20 kg/h feed and uses air as an oxidant compressed by a four staged reciprocating compressor. Both air and feed are electrically preheated before being introduced in the tubular mixers. Temperatures in the mixing point and in several points of the mixers are monitored. After leaving the mixer the reaction mixture is quenched. The products of the reactor are cooled in the intercoolers after leaving the reactor, and afterwards depressurization samples of the liquid and gas effluents can be taken. A flow diagram of the pilot plant is shown in Figure 1.

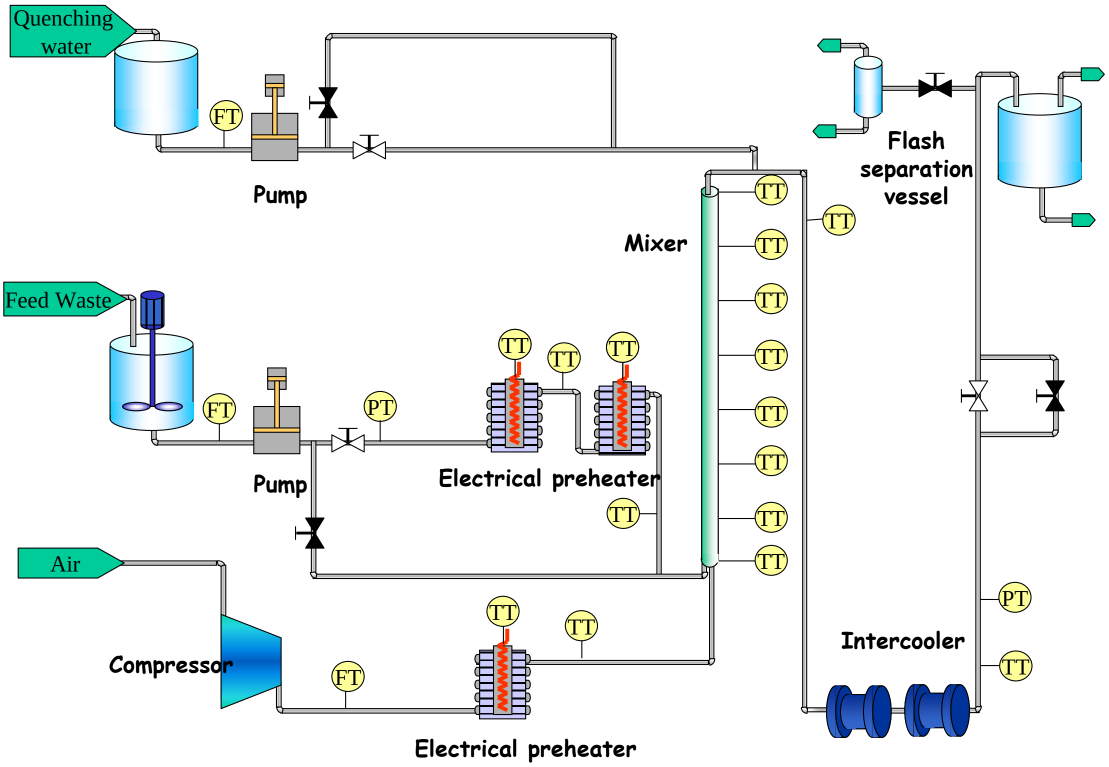

Figure 1. Flow diagram of the facility

The mixer was constructed with commercial Ni alloy C-276 tubing of ¼” (i.d. 3.86 mm). It consists of an upflow straight empty ¼” tube with a length of 1584 mm and an internal volume of 18.5 mL. Temperature was monitored using 8 thermocouples type K (temperature range from 0 to 1000 ºC) with accuracy of 1%. All of them have been thermally isolated.

All the feed used for the experiments consisted in synthetic solutions of isopropyl alcohol (IPA) (Technical 99% supplied by COFARCAS, Spain). Tap water was used without further purification. In all the experimental data the reagent mixtures (water + air) has been situated in the single phase region at the inlet of the mixer.

RESULTS AND DISCUSSION

Experiments in different feed flow rates and mixer injection temperatures were performed. It was observed that the temperature of the reaction mixture raised slowly until reaching a temperature certain temperature (around 450ºC) in which a rapid increase of temperature was observed. A typical temperature profile is shown in Figure 2

The temperature profiles were compared to the predictions of a model that considers a plug flow reactor in steady state. In the model only mass and energy balances were considered. Densities and enthalpies have been calculated as a function of composition and temperature using the PR EoS with the translated volume correction. The kinetic model developed by Li et al. [8] was used. It was found that the slow temperature rise of profile was reproduced while the subsequent rapid temperature increase was not. Comparison of the prediction of the model with experimental temperatures is shown in Figure 6.

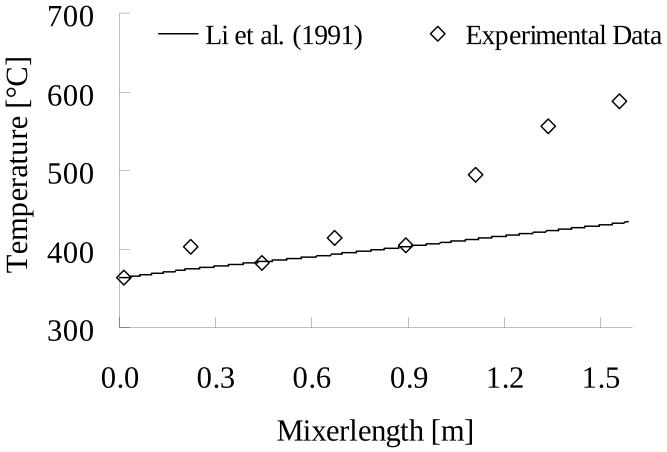

Figure 2. Comparison of a experimental temperature profile with the predictions of the kinetic model.

As all the mixers used were autothermal, the rapid increases of temperature were associated with a change in the reaction mechanism favored by the high temperatures. The phenomenon observed is very similar to the formation of hydrothermal flames described in literature [13-18].

TOC removal

Even when the object of this work was studying the reaction initiation and not obtaining total TOC removal, liquid samples were taken and TOC was analyzed. Almost complete TOC removals were obtained. The minimum TOC removals were of 55%, being the maximum residence times of 0.63 s. The data with higher TOC removal are associated with the ignition process. It is remarkable that even when the configuration of the mixers is not optimized for producing or sustaining a flame, total TOC removal can be obtained in residence times lower than 1 s. Oxidation by means of a hydrothermal flame makes possible the design of very small vessels for the SCWO process, what it is an important advantage in the industrial development of SCWO process.

CONCLUSIONS

An experimental study of the mixing process and reaction initiation has been carried out. The obtained conclusions are the following:

· The reaction initiation has been studied in a tubular mixer at different feed flows, IPA concentrations and inlet temperatures. All the experiments have been realized in the one phase region. Temperature profile inside the mixer has been used as the main indicating parameter.

· When the reacting mixture reaches a certain temperature (autoignition temperature) much rapid temperature increase was observed evidencing a faster reaction rate. These observations are consistent with the description of hydrothermal flames.

· Flameless experimental temperature profiles could be reproduced using the kinetic model developed by Li et al. Reaction rates when a flame is present are much faster that models described in literature.

· Totals TOC removals can be obtained in residence times lower than 1 s when ignition is produced.

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