

Experimental Study of the Hydrothermal Flame Formation and Behavior in a Vessel Reactor for Supercritical Water Oxidation

Pablo Cabeza, M. Dolores Bermejo*, Cristina Jiménez, Joao P.S. Queiroz, Arán Matías, M. José Cocero
High Pressure Process Group, Dept. Chemical Engineering and Environmental Technology, University of
Valladolid, C/ Doctor Mergelina s/n, 47011 Valladolid, SPAIN

Corresponding author, FAX: +34-983423013 , e-mail : mdbermejo@iq.uva.es

The supercritical water oxidation (SCWO) is a promising technology for the destruction of wastes, but its commercialization has been delayed by the problems of corrosion and salt deposition associated to this technology and as well for its high energetic consumes. Using reactors working with a hydrothermal flame as a heat source contributes to overcome many of the challenges presented by this technology. Injection of the reagents over a hydrothermal flame can avoid the reagents preheating as the feed can be injected into the reactor at low temperatures, avoiding plugging and corrosion problems in a preheating system. Also the kinetics is much faster allowing complete destructions of the pollutants in residence times much lower than 1 s. Next to this the high temperatures associated to the hydrothermal flames contribute to a better energy recovery of the reaction heat for electricity production. Since Franck and co-workers [1] discovered for the first time the existence of hydrothermal flames, several research groups has developed reactors working with a hydrothermal flame as a heat source [2, 3]. The High Pressure Process Group (HPPG) of the University of Valladolid (UVA) has developed several vessel reactors since 1993. It was proved that formation of hydrothermal flames was not possible in tubular reactors at temperatures lower than 350°C [4]. Thus, vessel reactors provide a space where the cold reagents are preheated to the autoignition temperature and brought into contact with the radical formed facilitating flame formation. In this work the ignition of hydrothermal flames is experimentally studied in a cooled wall vessel reactor. The influence of feed flow, injection temperature and geometry of the injection system has been evaluated by studying the temperature inside the reactor and the TOC removal.

INTRODUCTION

Supercritical water oxidation (SCWO) is a promising technology for the total destruction of wastes with residence times of a few seconds [1, 2] and even in residence times lower than one second if the reactor works in hydrothermal flame regime [3]. The formation of hydrothermal flames was discovered for first time by Franck and coworkers in the eighties [4]. Since Franck and co-workers discovered for the first time the existence of hydrothermal flames, several research groups have developed reactors working with a hydrothermal flame as a heat source [5, 6]. SCWO with a hydrothermal flame has a number of advantages; some of them allow overcoming the traditional challenges that makes difficult the successful and profitable commercialization of the SCWO technology. These advantages are the following:

- It allows the destruction of the pollutants in residence times of a few milliseconds allowing the construction of smaller reactors [7].
- It is possible to initiate the reaction with feed injections temperatures near to room temperature [5, 6, 8]. This last point supposes an advantage from the operational and the

energetic integration point of view, as avoid problems avoiding plugging and corrosion problems in a preheating system.

- Higher operation temperatures improve the energy recovery.

The High Pressure Process Group (HPPG) of the University of Valladolid (UVa) has developed several vessel reactors since 1993. Experimental results using a transpiring wall reactor demonstrated that once initiated the reaction it can be kept steady at temperatures as low as 110°C [8]. At that temperature the reaction was extinguished. The operational conditions used, concentrations of IPA of 6.5% wt and temperatures above 470°C situated the operation in the flame regime according of the results of Serikawa [9] ($C > 4\%$ wt IPA and autoignition temperature higher of 470°C). In fact when the maximum temperature in the reactor was under the autoignition temperature the flame was extinguished. At first, it was considered that reaction was initiated in the mixer/injector, and that the mixing was a key factor in the reactor design. Thus, experiments with different tubular static mixers outside of a reaction chamber were performed. These experiments were already described in literature [7].

For none of the mixers considered the flame could be kept steady at temperatures lower than 370°C, narrower or filled mixers presented worst results than a simple empty ¼” tube. Thus, it was proved that hydrothermal flames are formed outside the injectors and that a reaction vessel was more favorable than a tube for keeping a stationary hydrothermal flame at low injection temperature. In fact, vessel reactors have demonstrated to be more successful in maintaining steady stable hydrothermal flames with injection temperatures near to room temperature [5, 6, 8].

In this work the experimental parameters related to the formation using tubular cooled-wall reaction chamber. The influences of feed flow, injection temperature and diameter of the mixer were studied as well as the flame front velocity.

EXPERIMENTAL

All the results presented here were obtained in the pilot plant of the University of Valladolid. It has been previously described elsewhere [7-8]. In its present configuration it has a maximum treatment capacity of 24 kg/h and it uses air as oxidant. The reactor consists of a vertical Ni-alloy reaction chamber of 53.4 mm of internal diameter and 1 m high. It is inside of a reaction vessel made of AISI 316 able to stand a maximum pressure of 30 MPa and 400°C. Between the walls of the two vessels a stream of cold water refrigerates the reaction vessel. The reagents (feed and air) were introduced in the reactor through a tubular injector that ends in the top of the reactor chamber. The reaction was produced at the top of the reactor, where the maximum temperature was registered. The products flowed down the reactor leaving it by its lower part. Two injectors were tested. Both of them were made of commercial tubing 950 mm long. One of them had an external diameter of ¼ “ and 3.86 mm of internal diameter and the other 1/8” external diameter and 2.16 mm of internal diameter.

A number of experiments were performed. In every experiment, the reactor was first preheated electrically until the walls of the pressure vessel reached a temperature of 400° C. Then the reaction was initiated using IPA concentrations as high as 7.5% IPA and the electrical heating of the wall of the reactor was turned off. Several stationary states were reached while the injection temperature was decreased and samples were taken. For keeping the maximum temperature constant in values around 600-700°C the IPA concentration was increased as the injection temperature was decreased.

Temperatures were measured in several points of the reactor with thermocouples type K (temperature range from 0 to 1000 °C) with an accuracy of 1% of the measurement. The position of the temperature measurements T1 and T2 in the top of the reaction chamber are indicated in Figure 1. Air flow was measured with a Coriolis gas flow meter with a precision of 0.2%. To determine liquid flows, the time needed to pump a fixed volume was measured by the computer. IPA solutions were prepared volumetrically, measuring water volume with a precision of 1 L and IPA volume with a precision of 1 mL, resulting in an experimental error of 0.3-0.6% for a 6.5-12.5% IPA solution.

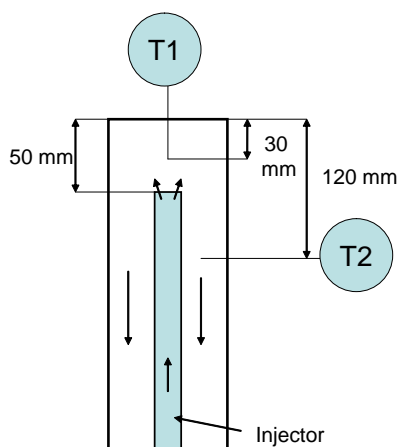


Figure 1. Scheme of the top of the reaction chamber, with the position of the injector and thermocouples

The experiments mentioned in this work were performed using synthetic feeds prepared with isopropanol (IPA, 99% purity) provided by COFARCAS (Spain) and water from the tap without further purification.

The Total Organic Carbon (TOC) of the samples was determined using a SHIMADZU TOC Analyzer model TOC-VCSH.

EXPERIMENTAL RESULTS

Experiments showed that the reactor could successfully destroy the IPA with efficiencies generally higher than 99.95% and TOC concentrations in the effluent of less than 20 ppm using both mixers. Feed injections temperatures (T_{Feed}) were progressively reduced and, at the same time, the IPA concentrations were increased in order to maintain a maximum temperature between 600 and 700°C, as observed in Figure 2.

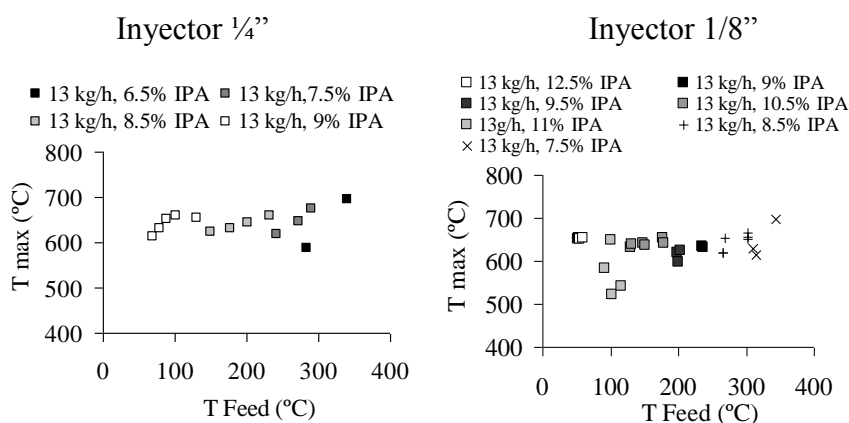


Figure 2. Maximum temperatures registered in the reaction chamber for different IPA concentrations for $\frac{1}{4}$ '' and $\frac{1}{8}$ '' mixers.

Steady operation was possible with feed temperatures lower than 100°C, and total TOC removal were also obtained in these conditions, as shown in Figure 3.

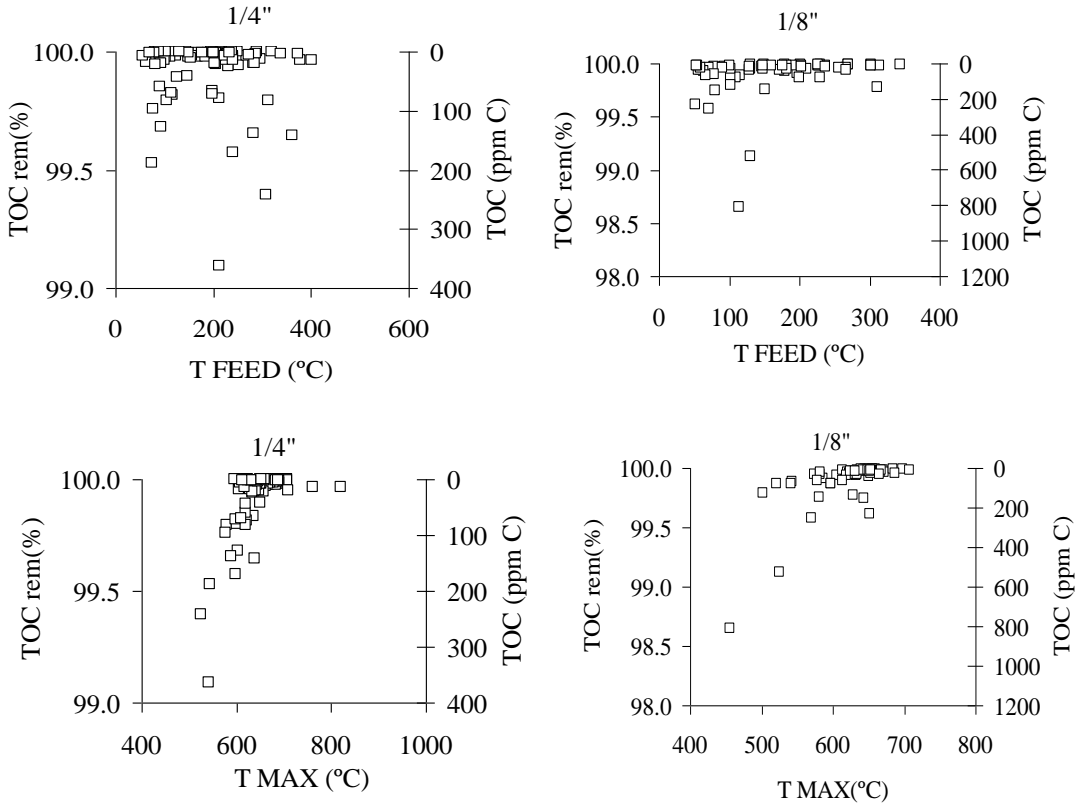


Figure 3. TOC removal (TOC rem.) and effluent TOC vs maximum reaction temperature (T MAX) vs Feed injection temperature for 1/4 and 1/8”mixers

Influence of the operational condition in the position of the flame front

It was observed that the maximum temperature was displaced from position T1 to position T2 when the feed temperature was decreased and the difference between these two temperatures become smaller again when IPA concentration is increased, as showed in Figure 4.

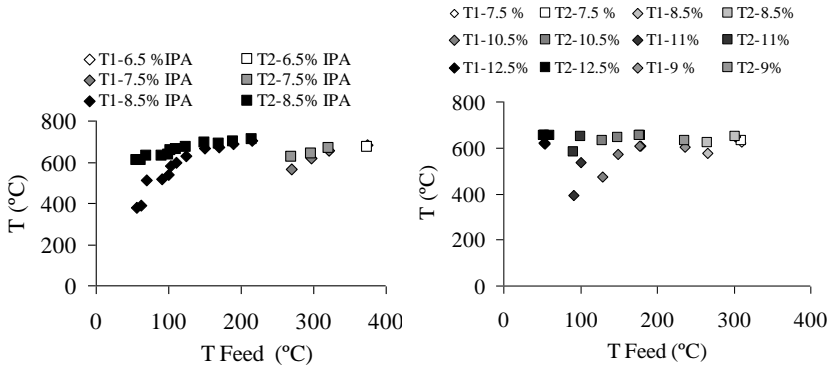


Figure 4. Temperatures T1 and T2 vs injection temperature for increasing IPA concentrations. a) Feed= 20 kg/h, injector 1/4”; b) Feed= 13 kg/h; injector 1/8”

The difference between temperatures T1 and T2 was also influenced by the velocity at the exit of the mixer. The influence of the velocity at the exit of the injector is made evident in Figure

5. The data of the temperature difference for different velocities is plotted against feed inlet temperature. The velocity has been calculated fixing a temperature of 350°C for the mixture at the outlet of the injector. The data present high degree of dispersion because of considering the same temperature for all the data and also because the concentration has not been taken into account, and it has some influence as shown in Figure 4. We notice that the difference between T1 and T2 was increased with decreasing feed inlet temperatures, and it is substantially higher when increasing the fluid velocity at the outlet of the mixer.

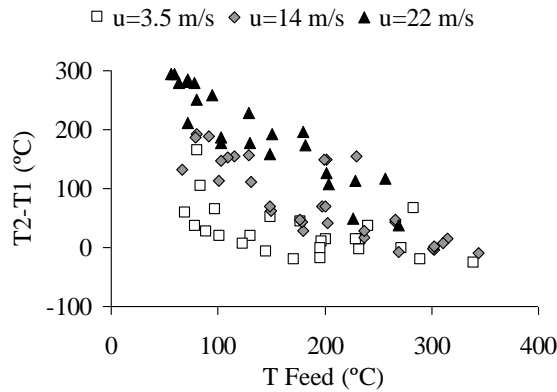


Figure 5. Temperatures difference (T1-T2) vs injection temperature for different velocities at the outlet of the mixer

This can be interpreted as that the hydrothermal flame front is displaced depending on the injection conditions. In order to try to understand this phenomenon the velocity of the flame front was estimated using the expression showed in equation (1) and developed by Mikhelson (1989) [10]:

$$v = \sqrt{\frac{\alpha}{\tau}} \quad (1)$$

Where α is the thermal diffusivity and τ is the characteristic time of the chemical kinetics. They are defined in equations (2) and (3).

$$\alpha = \frac{\lambda}{\rho \cdot c_p} \quad (2)$$

$$\tau = \frac{1}{k} = \frac{1}{A_0 \cdot \exp\left(\frac{-E_a}{RT}\right)} \quad (3)$$

Where,

λ is the thermal conductivity; ρ the fluid density; C_p the specific capacity of the fluid; k , the specific reaction rate; A_0 , the Arrhenius pre-exponential factor; E_a the energy of activation, R , the gas constant and T , the Temperature.

Properties were calculated assuming a temperature for the flame. Density and specific heat capacity were calculated using the Peng-Robinson EoS with the translated volume correction [11], taking the composition of the fluid before combustion. Pure water was admitted for the thermal conductivity. Kinetic parameters were experimentally determined from the data taken

from Bermejo et al [7]. At temperatures around 700°C and 23 MPa the flame front velocities are around 0.03 m/s, much lower than the typical flame front velocities in air combustion (0.4-3 m/s). Nevertheless this value can only be considered estimative because the equation considers the approximation of constant properties before and after the flame front. The velocities inside of the mixer are around 3-24 m/s and the velocities in the reaction chamber are around 0.1 m/s. Thus, it is expected that the flame front is maintained stationary in some point of the reaction chamber, where the flame front velocities are of the same order of magnitude that the velocity estimated for the flame front.

CONCLUSIONS

The behavior of hydrothermal flames in a reaction chamber using different tubular injectors inside a cooled reaction chamber was experimentally studied using two injectors of 0.95 m long and ¼” and 1/8” of diameter.

Stable hydrothermal flames were maintained at feed flows between 13 and 23 kg/h and feed injection temperatures lower than 50°C. High TOC removals were obtained in all the operational conditions with TOC concentrations of less than 20 ppm in the effluent.

The position where the higher temperature is registered was moving backward when increasing velocity and reducing feed injection temperature and fuel concentration.

Flame front velocity of the hydrothermal flame was estimated in 0.03 m/s, much lower than typical flame front velocities in conventional combustion. These velocities are lower than the velocity inside the injector (3-24 m/s) and of the same order of magnitude than those in the reaction chamber (0.1 m/s). Thus, it is expected that the flame is stabilized in the reaction chamber and not in the injector.

ACKNOWLEDGEMENT

The authors thank to Spanish Ministerio de Medio Ambiente (project 346/PC/08/3-04.3) and BEFESA AGUA, S.A.U. M.D.B. thanks the program Juan de la Cierva (JCI-2008-02877) funded by the Ministerio de Ciencia e Innovación (Spain).

REFERENCES

- [1] BERMEJO, M.D., COCERO, M.J. *AIChE J.*, Vol. 52, **2006**, p. 3933
- [2] BRUNNER, G. *J. Supercrit. Fluids*, Vol. 47, **2009**, p. 382
- [3] AUGUSTINE, C.; TESTER, J.W. *J. Supercrit. Fluids*, Vol. 47, **2009**, p. 415
- [4] SCHILLING, W; FRANCK, E.U. *Ber. Bunsenges. Phys. Chem.*, Vol. 92, 1988, p. 631
- [5] OH, C.H.; KOCHAN, R.J.; CHARLTON, T.R.; BOURHIS, A.L. *Energy Fuels*, Vol. 10, **1996**, p. 326
- [6] WELLIG, B.; WEBER, M.; LIEBALL, K.; PRIKOPSKY, K.; RUDOLF VON ROHR, PH. *J. Supercrit. Fluids*, Vol. 49, **2009**, p. 59
- [7] BERMEJO, M.D.; CABEZA, P.; BAHR, M.; FERNÁNDEZ, R.; RÍOS, V.; JIMÉNEZ, C.; COCERO, M. J. *J. Supercrit. Fluids*, Vol. 50, **2009**, p. 240
- [8] BERMEJO, M.D.; FDEZ-POLANCO, F.; COCERO, M.J. *J. Supercrit. Fluids*, Vol. 39, **2006**, p. 70
- [9] SERIKAWA, R.M; USUI, T.; NISHIMURA, T.; SATO, H; HAMADA, S.; SEKINO, H. *Fuel*, Vol. 81, **2002**, p. 1147
- [10] MIKHELSON, V. A., Ph.D. Thesis, Moscow University, Moscow, **1989**
- [11] MAGOULAS, C., TASSIOS, D. *Fluid Phas. Equilib.*, Vol. 56, **1990**, p. 119
- [12] SHIH, T.H., LIOU, W.W.; SHABBIR, A., YANG, A., ZHU, J. *Computers Fluids*, Vol. 24, 1995, p. 227