SUPERCRITICAL WATER OXIDATION OF INDUSTRIAL WASTE WATER FROM PILOT TO DEMONSTRATION PLANT

M.J. Cocero *, A. Martín, M.D. Bermejo, M. Santos, D. Rincón, E. Alonso, F. Fdez-Polanco

University of Valladolid, Chemical Engineering Department

C/ Prado de la Magdalena S/N. 47011 Valladolid (SPAIN)

Fax: +34 983 423013, e-mail: mjcocero@iq.uva.es

ABSTRACT

Supercritical water oxidation (SCWO) has demonstrated to be a powerful technology for the treatment of wastewater containing organic matter. The commercial development of this technology goes mainly through engineering considerations. Previous results of the research group provide the pilot plant operating conditions used in the design of the reactor and energetic studies. These operating conditions are reaction temperature of 650ºC, pressure of about 25 MPa, and the stechiometric proportion of oxygen, independently of the nature of the waste.

The good results obtained with the operation have allowed the construction of a demonstration plant in the site of the waste - treatment company CETRANSA in Santovenia de Pisuerga (Valladolid). This plant has a treatment capacity of 200 kg/h. it uses pure oxygen as oxidant, and operates at 650ºC and 25 MPa. A new cooled wall reactor has been designed from the scale-up of the pilot reactor. Solids are separated before going into the reactor by precipitation in a settle device. In this paper, the scale –up studies from the pilot to the demonstration plant are presented.

INTRODUCTION

Since the pioneer work of M. Modell in the 80`, supercritical water (SCW) has become an alternative medium for chemical reactions, mainly chemical oxidation processes [1]. SCW has several advantages over the incinerations and the wet oxidation processes which makes it more environmentally benign that those processes. Together with these advantages, oxidation in supercritical water has disadvantages associated to operation at high-pressure temperature, and oxidant atmosphere [2]. These disadvantages are corrosion and salts precipitation. So, nowadays SCWO is not a general technology for all kind of waste-streams [3].

SCWO can be a technical and economical solution for wastes with high concentration of organics and non-biodegradable compounds with low concentrations of hallogenated compounds. This industrial application needs a robust, versatile and economic process [4].

In order to develop an end-of-pipe technology, the Department of Chemical Engineering of Valladolid University has developed a demonstration supercritical water oxidation plant with a treatment capacity of 200 kg/h of wastewater, using oxygen as oxidant. From pilot plant experimental results and energetic studies, the scale-up of the process has been developed. A cooled wall reactor with a design mixer has been built with the objective of performing long time test with industrial wastewater. This plant started to work in January 2003.

This paper presents the scale-up of the reactor and the main features of this plant.

PILOT PLANT RESULTS

The SCWO pilot plant has a treatment capacity of 30 kg/h working with air as oxidant and 70 kg/h working with oxygen. The main features of the pilot plant have been published in previous papers [5]. This pilot plant has been under operation since 1998 until 2001 in order to get design values for the main equipment of the demonstration plant [5, 6].

The cooled wall reactor of the pilot plant has been scaled-up to develop the new reactor. It uses the feed stream to cool down the wall of the reactor at the same time that the feed stream is preheated An operation temperature of 700ºC can be achieved with reactor wall temperatures below 400ºC. Chemical corrosion is reduced and reactor wall thickness can be reduced, thus getting an economical design alternative for moderate salt concentrations. Figure 1 shows the relationship between reaction temperature and oxidation yield for a synthetic waste with isopropyl alcohol concentrations between 6 – 7 wt%, working with oxygen as oxidant:

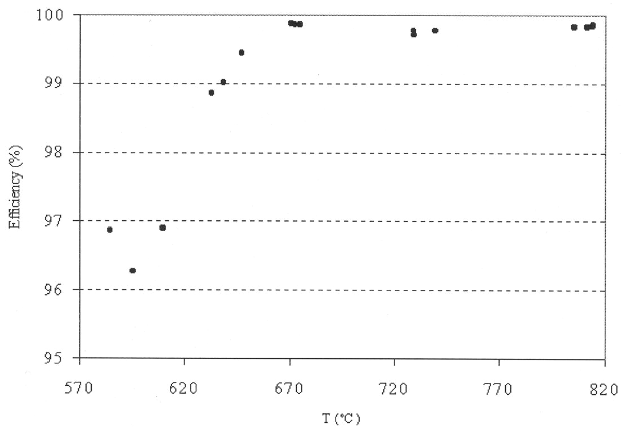

Figure 1 Oxidation yield vs. reaction temperature

Previous experimentation allow to select the following operating conditions: temperature of 650ºC, pressure of 23 MPa, residence time of 50 s, stechiometric amount of oxidant, and 930 kJ/kg heating value in the feed stream to run an energetically self-sufficient operation [7].

REACTOR MODELLING AND SCALE-UP

A mathematical model of the reactor has been developed in order to scale – up the reactor and optimize the process using the most adequate variables, conditions and configuration for this particular reactor. A detailed description of the model can be found elsewhere [8].

Figure 2 shows experimental reactor temperatures and simulated temperature profiles for a solution of 6 wt% of isopropyl alcohol using oxygen as oxidant. One curve corresponds to the temperature profile inside the reaction chamber, and the second curve represents the temperature profile of the pressure shell. The oxidation reaction is extremely fast, therefore there is an enormous release of heat at the first stages. This causes a sharp increase of the reaction temperature.

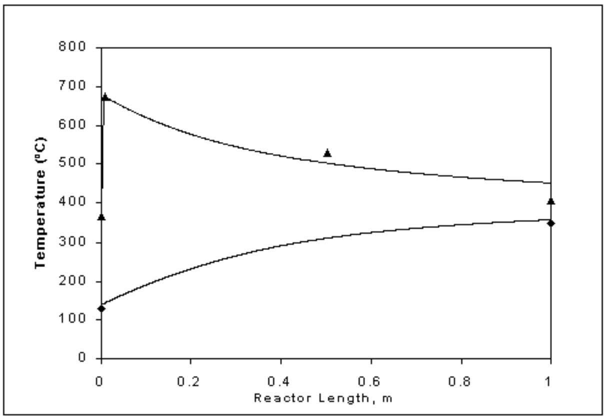

Figure 2: Temperature profile using oxygen and 6.5 wt% of isopropyl alcohol (fuel)

Due to the formation of reaction intermediates, even if the oxidation of organic pollutants is almost complete in the first centimeters of the reactor, the TOC removal is not total at the outlet. The total amount of acetic acid produced depends on the initial concentration of organic matter of the fuel, and thus on the reaction temperature. Lower concentrations in the feed lead to lower amounts of intermediates, but their upcoming degradation is inhibited since lower temperatures are reached. The total degradation of acetic acid cannot be carried out in the reactor if a minimum reaction temperature is not reached, as it is shown in Figure 3.

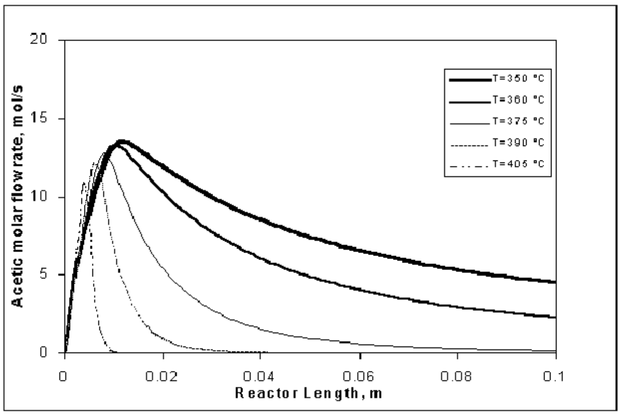

Figure 3: Sensitivity analysis versus initial temperature for the formation and degradation of acetic acid.

Simulations with a constant fuel quantity show that the maximum reaction temperature is strongly sensible to the reactor inlet temperature. A variation of 50ºC in the initial temperature generates a difference of more than 200ºC in the maximum reaction temperature, as it is shown in Figure 4. For that reason, it is recommended to preheat the feed to temperatures higher than the critical temperature of water. The experimental results obtained with the pilot plant confirm this conclusion.

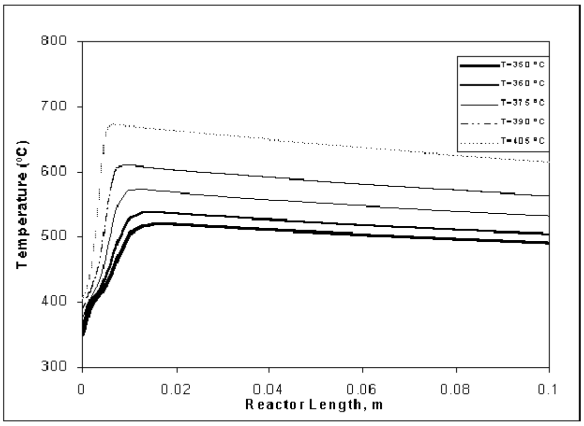

Figure 4: Sensitivity of reactor initial temperature

COOLED – WALL REACTOR

The mechanical design of the Cooled-Wall Reactor has been carried out using the AD – Merkblätter Standards. Figure 5 presents an explicative diagram of a cooled – wall reactor. In this type of reactor temperature and pressure effects are isolated by using a stainless – steel cooled wall pressure vessel, which is maintained at a temperature below 400º C, and inside it, an inconel reaction chamber, which does not support pressure, where reactants are mixed and reaction takes place. This way, pressure stress, and temperature and corrosion stresses are supported by different parts of the reactor.

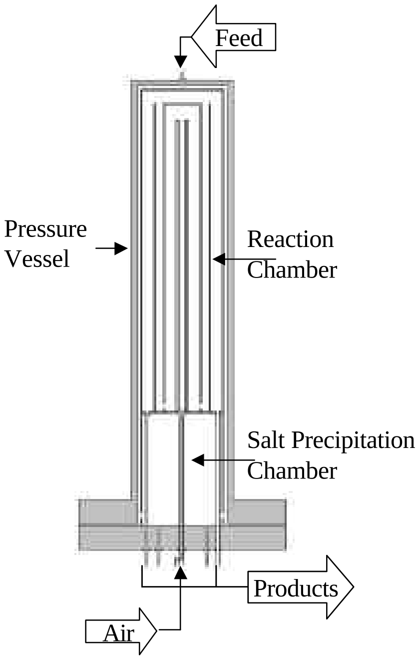

Figure 5: Diagram of the cooled wall reactor of SCWO demonstration plant

The reactor works as follows: the cold feedstream enters in the top of the pressure vessel, and flows down the space between the pressure vessel and the reaction chamber, being heated by the reaction heat until supercritical conditions. On the bottom the feed stream enters the reaction chamber through a salt precipitation chamber, where the salts contained in the feedstream precipitate. Then the feed stream is forced to enter in the mixer togheter with the oxygen that enters in the reactor by the bottom. After going out the mixer, where most of the reaction takes place, the products of the reaction pass through a serie of chambers where the products cool down transferring heat to the feed stream, before leaving the reactor. It is also possible to introduce the cold feed directly in the mixer. This is a safety device which allows to cool and stop the reaction if necessary. The effective reaction volume of this reactor is of 13.6 L

SCWO DEMONSTRATION PLANT

The basic flowsheet of the demonstration plant situated in the site of the firm CENTRANSA in Santovenia de Pisuerga, Valladolid (SPAIN) is presented in Figure 6. The main items of this facility are described below:

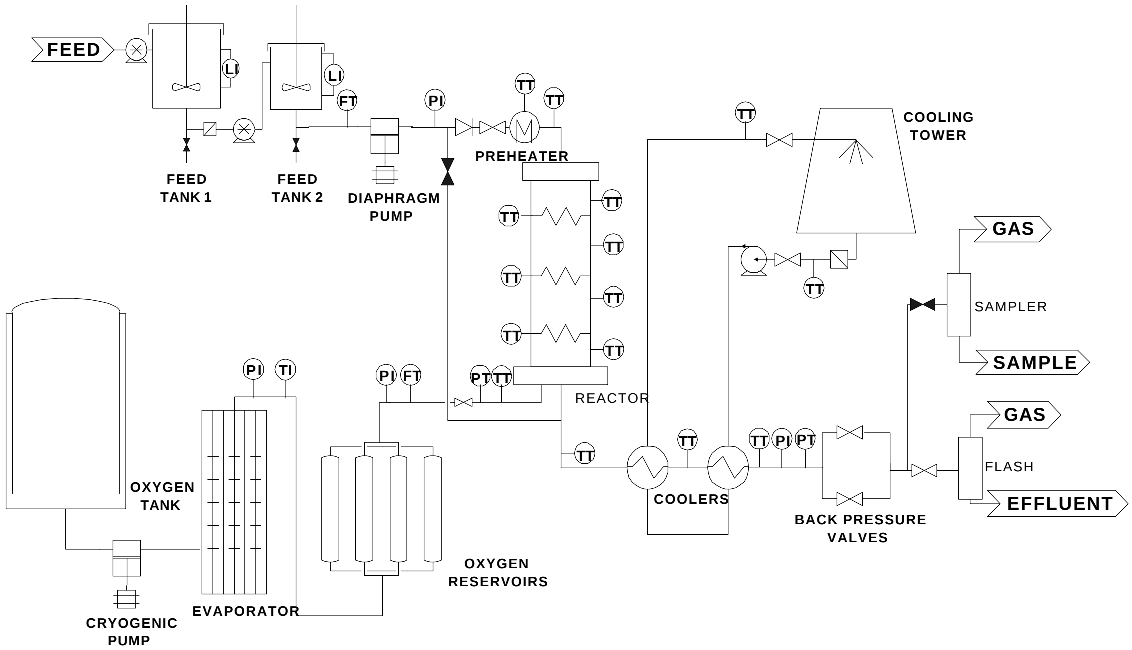

Figure 6: Flowsheet of the SCWO demonstration plant

- Feed streams conditioning equipment. It consists of a tank where the feed is prepared paying special attention to the concentration of organic matter, because this concentration determines the operating temperature of the reactor. From this tank the feed is driven to the feed tank, from where it is pumped with a metering diaphragm pump (DOSAPRO MAX ROYAL C) until work pressure (23 MPa). In this line also exists an electrical 10 kW preheater, used to preheat the feed in the start up of the reactor.
- Oxygen supply facility. The oxygen is supplied by Carburos Metalicos S.A. Liquid oxygen is stored in a cryogenic deposit, from where it is pumped by a cryogenic metering pump until work pressure. After pumping, oxygen is vaporized in a finned tube unit. Then it is stored in four reservoirs before mixing it with the aqueous waste stream, in order to vary oxygen flow.
- The cooled-wall reactor described before
- Cooling systems. They consist of two coolers, in which the hot product of reaction flows inside a titatium alloy (Ti – 3Al – 2,5V) coil, and is refrigerated by water, that is cooled in a cooling tower.
- Back pressure regulator valve: A needle valve, SENTRY VREL11, is used. For security reasons, a second valve is placed in parallel to this valve.

- Flash chamber separator: in this chamber, the liquid and gaseous parts of the effluent are separated. In parallel to this flash separator, a sampling device allows to take samples of the liquid and gaseous effluents.

A picture of the demonstration plant is presented in the Figure 7

Figure 7: Picture of the SCWO demonstration plant

CONCLUSION

A demonstration plant for the SCWO process has been developed for the treatment of industrial wastewater. This plant has a treatment capacity of 200 kg/h, uses oxygen as oxidant, and operates at 650ºC and 25 MPa. A new cooled wall reactor has been built from the scale – up of a pilot reactor. An operation manual has been developed in order to achieve adiabatic conditions in the reactor in the steady – state operation of the plant.

REFERENCES

[1] MODELL M., "Supercritical Water Oxidation" in the book "Standard Handbook of Hazardous Treatment and Disposal" H.M. Freeman ed. McGraw Hill, **1988**.

[2] COCERO, M.J. "Supercritical Water Oxidation. Applications to Wastewater Treatment." 566-599 High Pressure in Chemical Engineering. Fundamentals and Applications. A. Bertucco, G. Vetter Eds. Elsevier, **2001** , p. 566.

[3] KRITZER P. DINJUS E.. Chem. Eng. J, Vol 83, **2001**, p 207.

[4] GIDNER A., STENMARK L., ABRAHAMSSON J., CARLSSON K., The Chematur Engineering SCWO pilot plant. Treatability studies, Proceeding of the 6th Meeting on Supercritical Fluids.- Chemistry and Materials.- Nottingham (U.K.), **1999**, 427

[5] COCERO, M.J.; ALONSO, E.; VALLELADO, D.; TORÍO, R.; FDZ-POLANCO, F. Ind. Eng. Chem. Res., Vol 39, **2000**, p. 3707

[6] COCERO M. J. , E. ALONSO, D. VALLELADO, R. TORIO, F. FDEZ- POLANCO. Ind. Eng. Chem. Research. Vol 39(12), **2000**, p. 4652.

[7] COCERO, M.J.; ALONSO, E.; SANZ, T.; FDZ-POLANCO, F. J. Supercrit. Fluids, Vol 24, **2002**, p 37.

[8] COCERO M. J., MARTINEZ.J. L. "Cool wall reactor for supercritical water oxidation. Modeling operation results". Submitted to the Journal of Supercritical Fluids, **2002**.