

ION EXCHANGE RESINS DESTRUCTION IN A STIRRED SUPERCRITICAL WATER OXIDATION REACTOR

A.Leybros¹, A. Roubaud¹*, P. Guichardon², O. Boutin², B. Fournel¹

¹ CEA Valrhô, DEN/DTCD/SPDE/Laboratoire des Fluides Supercritiques et Membranes, BP111, 26702 Pierrelatte Cedex, France

² UMR CNRS 6181 Laboratoire des Procédés Propres et Environnement, Europôle de l'Arbois BP80, 13545 Aix en Provence Cedex, France
Email: anne.roubaud@cea.fr

Spent ion exchange resins (IER) are radioactive process wastes for which there is no satisfactory industrial treatment. Supercritical water oxidation could offer a viable treatment alternative to destroy the organic structure of resins and concentrate radionuclides in the liquid phase. Up to now, IER degradation rates higher than 99% were difficult to obtain even using a catalyst or a large oxidant excess. Within the double shell reactor, a co-fuel, isopropyl alcohol has been used to improve degradation rates. Total Organic Carbon reduction rates higher than 99% were obtained thanks to this process, and results are significantly better than those obtained with suspensions of water + ion exchange resins.

INTRODUCTION

Above its critical point ($T > 673$ K and $P > 22.1$ MPa), water undergoes significant modifications of its properties, like a dropping down of dielectric constant and thermal conductivity. Thus, supercritical water acts as a homogeneous non polar solvent with high diffusivity and high transport properties. Oxidation reactions are fast in the case of a water-organic-oxidant mixture without interfacial transport limitations. Such destruction reactions are total and lead to the conversion of organic compounds into CO_2 and H_2O . Hence, the supercritical water oxidation process is very efficient to treat organic wastes.

Nevertheless, the operating conditions lead to two well-known problems: corrosion and salt precipitation. The stirred double shell reactor, developed by the CEA Valrhô, overcomes this problem. A stainless steel vessel withstands pressure and a titanium inner tube confines the aggressive media. Moreover, a stirrer keeps salts in suspension and improves heat transfer [1]. Polystyrenic ion-exchange resins (IER) are widely used for water treatment in nuclear power plants. Spent resins are radioactive wastes for which there is no satisfactory industrial treatment. Various treatments such as pyrolysis/incineration, electrochemical oxidation and coating [2] have been studied. A few studies were made concerning destruction of IER by Supercritical Water Oxidation [3-5]. It could offer a viable treatment alternative to destroy the organic structure of the resins and concentrate radionuclides in the liquid phase.

Isopropyl alcohol oxidation can lead to hydrothermal flames. Serikawa and coll. [6] observed a spontaneous ignition of flames within a short period after the oxidant injection. A map of the ignition limits has been provided for isopropylalcohol/water.

Several wastes have been oxidized using isopropylalcohol as a co-fuel, such as dioxins [6], industrial wastes [7] or nitrogenous compounds [8]. Results show that total removal is possible, even at high wastes concentrations.

The objective of this work is to investigate the supercritical water oxidation of ion exchange resins with and without the use of a co-fuel, isopropyl alcohol (IPA). This study shows the effect of several operating parameters on degradation rates of IER.

MATERIALS AND METHODS

The reactor (**figure 1**) is composed of a horizontal high pressure autoclave made with 316 stainless steel [1]. Along an half of it, four electric heaters (0.5 kW each) are disposed, followed on the other part by a cooling shell.

Within the autoclave, a thin titanium tube of 1 m length is placed so that the incoming flow of water and oxidant must reach by the outer part of it the opposite side of the reactor, where the waste is introduced. This tube protects the outer wall of the autoclave from corrosion. Pure water and oxidant (synthetic air O_2/N_2 at 20%/80% in volume) are introduced in the annular zone at ambient temperature. Air is pressurized by a compressor and water by a pump. Reaction takes place near the injection zone [9].

In the inner part of the tube, a titanium stirrer is placed in order to maintain a turbulent flow along the whole reactor. It enhances the heat and mass transfers and also prevents the precipitated salts from decanting in the “supercritical zone” and brings them in the subcritical zone of the reactor where they are dissolved again.

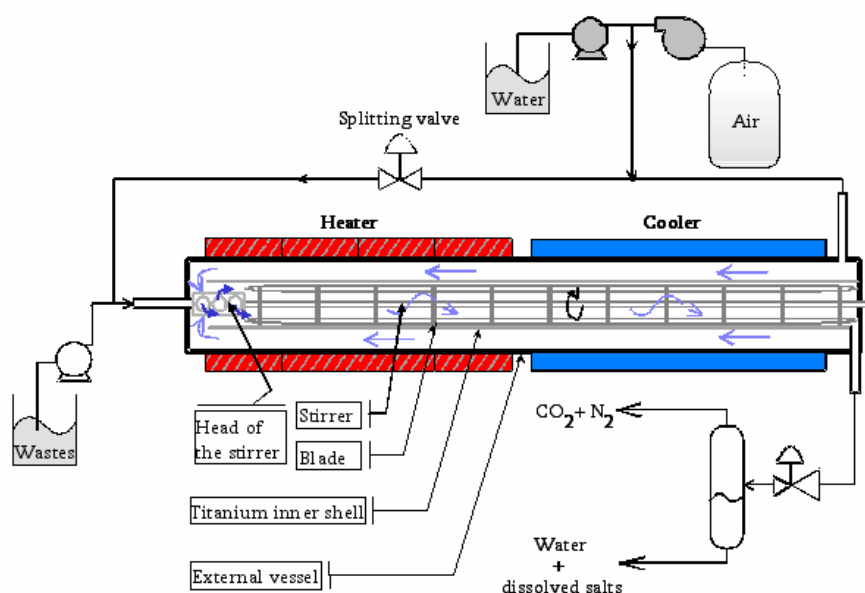


Figure 1: Description of supercritical water oxidation process

After phase separation, liquid and gas samples are obtained. The gaseous stream is analysed by a gas analyzer. We can thus measure volumetric concentrations of CO_2 , CO (by infrared spectroscopy) and O_2 concentrations (by paramagnetic system). The liquid phase is analyzed by a Total Organic Carbon Analyzer to determine the residual organic compounds concentration.

Most of the IERs used in nuclear power plant are strong acid-cation exchangers and strong base-anion exchangers. The resins used in these experiments (Amberlite IRN77 & Amberlite IRN78) are based on a styrene-divinylbenzene copolymer. They are manufactured by Rohm & Haas. Both resins are supplied in the form of beads (mesh size = 0.3-1.2 mm). Their characteristics are given on **table 1**.

| | Amberlite IRN77 | Amberlite IRN78 |
|--|-----------------|-----------------|
| Nature | Cationic IER | Anionic IER |
| Exchange capacity (equiv.L ⁻¹) | 1,8 | 1,1 |
| Density (g.L ⁻¹) | 800 | 650 |
| Moisture content (%) | < 55% | < 60% |
| Degree of cross-linking (DVB)(%) | 8 | 8 |
| Structure | | |

Table 1: Properties of ion-exchange resins

IER are crushed and sifted in order to have a particle size lower than 200 microns. A magnetic stirrer is used to avoid sedimentation in the feeding vessel.

RESULTS AND DISCUSSION

Initiation of IPA oxidation reaction. First, ignition conditions of IPA flames and resulting temperatures must be set. The inlet organic concentration and oxidant stoichiometry are found to be the most important parameters for the ignition of flames. Sporadic temperature peaks are observed when IPA dilution ratio is higher than 8% and air ratio is higher than 1.8. Continuous stable temperature is observed when air ratio is between 1.4 and 1.8. The flames ignite spontaneously when injection temperature is higher than 350°C. This temperature is found to be the minimum temperature necessary for the ignition of hydrothermal flames. The temperatures easily achieved extremely high value (~ 600°C for continuous flames and 800-900°C for sporadic flames).

With POSCEA experimental set-up, isopropylalcohol has been used to improve degradation rates by initiating the oxidation reaction and increasing temperature of the reaction medium.

Experimental results of IER degradation rates. Several tests were performed increasing the cationic or anionic resins content of the feed (up to 20%). For these experiments, conditions were set so that air ratio is greater than 1.2 and IPA dilution ratio is equal to 10%. TOC removal has been studied systematically (**Table 2**).

| Concentration (%wt) | | | water | IPA | resin | final TOC (mg/L) | Mean degradation rate (%) |
|---------------------|----|----|-------|-----|--------|------------------|---------------------------|
| 5 | 10 | 20 | | | | | |
| X | | | | X | IRN 77 | 0,5-7,5 | 99,99 |
| X | | | | X | IRN 78 | 12-43,5 | 99,95 |
| | X | | X | | IRN 77 | 44-95 | 98,75 |
| | X | | | X | IRN 77 | 15-32,5 | 99,97 |
| | X | | | X | IRN 77 | 65,5-318,5 | 99,7 |
| | X | | X | | IRN 78 | 148,5-221,5 | 98 |
| | X | | | X | IRN 78 | 56-139 | 99,9 |
| | | X | X | | IRN 77 | 243,5-377 | 95,85 |
| | | X | | X | IRN 77 | 94-177 | 99,85 |

Table 2: Ion exchange resins degradation results with or without isopropylalcohol

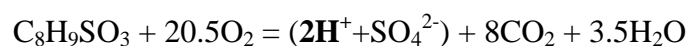
The use of IPA as a co-fuel allows to improve significantly degradation rates in comparison with the results for the {water + REI} mixture. These results are better than those found in the literature without using any catalyst or strong stoichiometric excess of oxidant. So, we can deduce that the effect of temperature increase is preponderant (**table 3**).

| | Experimental conditions | Degradation rate |
|-----------------------------|---|--|
| <i>Dubois and coll. [3]</i> | Temperature : 380-435°C Pressure : 220-260 bar O ₂ stoichiometric excess | Reaction time : 1-60 min Concentration : 1,5-5g/L Batch reactor |
| <i>Sugiyama and [4]</i> | Temperature : 400-450°C Pressure : 310-430 bar Catalyst : RuO ₂ | Reaction time : 5-180 min Concentration : 5% wt Batch reactor |
| <i>This study</i> | Temperature > 600°C Use of IPA as a co-fuel Pressure : 300 bar | Concentration : up to 20%wt O ₂ stoichiometric excess Continuous flow reactor |

Table 3: Effect of the temperature on degradation rates

Experiments were made up to 20%wt ion exchange resins concentration in water and in isopropylalcohol. Thanks to TOC measurements, we can observe that there are significant differences between degradation rates with and without isopropylalcohol (**Table 2**). Except for water + 20% REI, no solid residues were observed in the liquid samples.

Degradation rates of cationic resins are higher than those of anionic resins. It is due to the presence of some functional groups in the resins. Bonding energy of C-S is weaker than bonding energy of C-N and C-C. So, breaking bonding of the functional groups requires more energy, which explains lower degradation rates. Moreover, for cationic resins, low pH (around 2) is a good degradation reaction indicator, because of release of H⁺ ions:



Eq.1

Sulfur conversion. The experiments indicate that sulfur contained in the particles is oxidized to sulfates in supercritical water medium. In the literature [10], the main species containing sulfur in the effluents are transformed into sulfides, thiosulfides, sulfites and sulfates. In order to confirm this hypothesis, ionic chromatography analyses have been conducted. For the same concentration in ion exchange resins, we observe that sulfates concentration is much higher, with the use of isopropylalcohol (IPA) than in the case of suspensions of ion exchange resins in water. It confirms the results obtained by Wang and coll. [10]. They showed that it is possible to completely convert the sulfur present in the resins into sulfates by SCWO using high temperature ($T > 673$ K in the injection zone) and an extended reaction time.

CONCLUSION

The complete oxidation of suspensions of ion exchange resins with concentrations up to 20% wt in supercritical water has been studied using isopropylalcohol (IPA) as auxiliary fuel and air as oxidant. Complete removal (degradation rates greater than 99%) has been obtained after initiating the IPA combustion reaction, increasing the reactivity of the medium, whereas solid residues and lower degradation rates were observed for suspensions of ion exchange resins in water.

However, the experimental conditions with isopropylalcohol lead to the ignition of hot and sporadic or weak and continuous hydrothermal flames. Difficulties were observed for getting stable conditions. Another co-fuel may be used to reduce this effect.

The determination of intermediate species in liquid effluents by CPG-MS will give us additional information that may be useful in order to build global mechanisms.

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