Direct Injection of Oil Waste in a Supercritical Water Oxidation Reactor at Pilot Plant Scale

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Several industrial wastes are difficult to treat by Supercritical Water Oxidation SCWO since they are not soluble in water at room temperature, leading to different procedure problems related to pumping and preheating in the aqueous feed stream. This work describes a new system suitable to treat non water-soluble wastes in a pilot plant that includes three independent feed streams: 1) an aqueous feed stream, 2) a feed stream containing the non water-soluble waste (i.e. oil waste) and 3) an air stream added before entering the tubular reactor. Once the oxidant and the organic compounds are mixed at high temperature, the oxidation reactions take place at a high rate, releasing an important amount of heat. With an adequate control of these feed streams, this technological solution would extend the versatility of the SCWO process in respect of the concentration of residues to be treated (normally limited to between 5 and 20% organic matter), since it allows the combined treatment of diluted residues (<5%) in the aqueous feed and very concentrated residues (close to 100%) in the non-aqueous feed. The concentration desired in the reactor can thus be controlled, making it possible for the plant to remain self-sufficient in energy, or to generate surplus energy.

This paper study the best procedure and operating conditions to mix those three streams (water-oil-air) leading to both safe and efficient performance of a process where oxidation reaction that take place at a high rate, releasing an important amount of heat.

INTRODUCTION

Under most of current legislations, used oils are considered hazardous wastes and its safe collection and disposal must be ensured. Since conventional treatment methods are often inefficient or environmentally unacceptable, the development and application of new technologies is highly necessary. Complete elimination of oily wastes by hydrothermal oxidation could be an interesting alternative to conventional methods since it is an effective and environmentally clean technology.

SuperCritical Water Oxidation (SCWO) is a powerful emerging technology useful to eliminate a wide range of problematic wastes from a wide variety of chemical industries [1]. This technology is based on oxidation of wastes in an aqueous medium at pressures and temperatures above the critical point for pure water (374 ºC and 22 MPa, respectively). In those cases that the waste is not water-soluble at ambient temperature, conventional SCWO plants are not prepared to carry out the treatment in a proper way.

This work describes a new system suitable to treat non water-soluble wastes in a pilot plant scale.

MATERIALS AND METHODS

A supercritical water oxidation pilot plant to be operated up to 280 bar and 700ºC was built at the laboratories of the University of Cádiz. The pilot plant was design to be able to treat both wastewater and wastes not water-soluble at room temperature. Because it was designed to operate auto-thermally, the heating capacity of the effluent of the reactor is used to increase the temperature of the waste and the oxidant before they are mixing at the beginning of the reactor. Moreover, the SCWO pilot plant includes an electrical heating system in order to supply energy demand as in the case of the starting of the experiments. Due to the extreme work conditions, several safety components were included in the design and construction of the pilot plant. Fig. 1 shows a schematic diagram of the pilot plant facility.

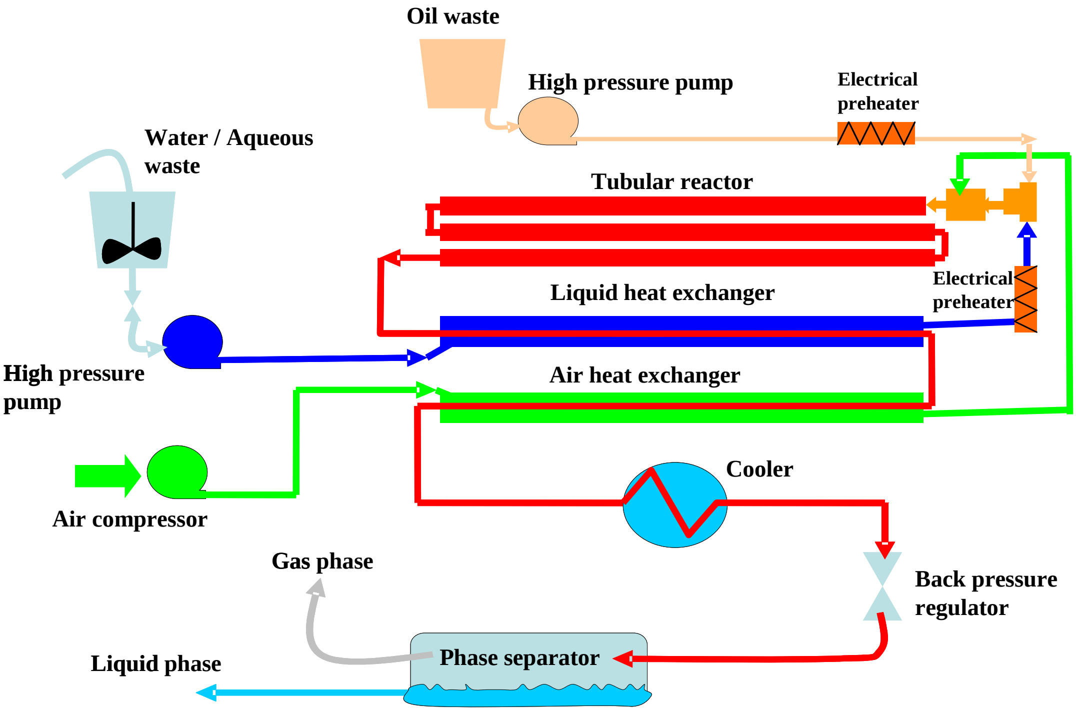

Figure 1: Schematic diagram of the SCWO Pilot Plant located at University of Cádiz.

This pilot plant facility includes three independent feed streams: 1) An aqueous feed stream (with or without organic contaminants) is pressurized by a high pressure liquid pump, preheated at supercritical temperature (above 400ºC) and introduced into the system at a flow rate up to 25 kg/h. 2) A second high pressure liquid pump is used to introduce continuously a new feed stream containing the non water-soluble waste (i.e. oil waste). This second feed stream is pressurized and mixed (with or without preheating) with the supercritical aqueous feed stream that dissolves completely the oily compounds. 3) A pressurized and preheated air stream added before entering the tubular reactor. Once the oxidant and the organic compounds are mixed at high temperature, the oxidation reactions take place at a high rate, releasing an important amount of heat. With an adequate control of these feed streams, this technological solution would extend the versatility of the SCWO process in respect of the concentration of residues to be treated (normally limited to between 5 and 20% organic matter), since it allows the combined treatment of diluted residues (<5%) in the aqueous feed and very concentrated residues (close to 100%) in the non-aqueous feed. The concentration desired in the reactor can thus be controlled, making it possible for the plant to remain self-sufficient in energy, or to generate surplus energy. In the event of overpressure and excessive temperature in the system, the feed without water (and therefore, more concentrated) is detained, while the entry of the aqueous flow is maintained; this enables safe conditions to be re-established, without it being necessary to shut-down the plant completely. The system and procedure included in this work is under patent [2].

RESULTS

The process has been applied to the treatment of Biocut®, a commercial semi-synthetic cutting oil that our research group has studied previously [3]. This oil is normally diluted between 2 and 10% v/v with deionized water to obtain a stable and homogeneous emulsion that is used in tooling machines to dissipate heat and to provide lubrication between the face of the cutting tool and the metal being cut. This oily fluid is a mixture of several compounds so the efficiency of the oxidation process was followed in terms of the reduction in chemical oxygen demand (COD). The oxidation reaction takes place at a high rate, releasing an important amount of heat depending on the initial concentration entering the reactor. As reactor is isolated, temperature goes increasing along reactor. The profiles of temperature and the maximum value of temperature into the reactor are depending on several operating parameters as the flowrates of the streams, the temperature of preheating of the stream, the concentration of the organic matter entering the reactor, etc.

Several experiments were carried out in the SCWO pilot plant in order to study the best procedure and operating conditions to mix those three streams (water-oil-air) leading to both safe and efficient performance of the process. Some of those operating parameters we had kept constant in experiments and other ones with variable values. The pilot plant it allows to manipulate and to control all of them in a wide range of values. In the present work we present the results obtained with the following operating parameters that showed good results from an operative point of view:

- temperature of water stream at the end of the electrical preheater before mixing with the oil feed: Tw, variable in experiments
- temperature of the oil stream at the end of the electrical preheater before mixing with water: To, around 100 ºC in all experiments
- flow rate of water stream: around 12 kg/h in all experiments
- flow rate of oil stream: around 2 kg/h in all experiments
- flow rate of air stream: around 190 g/min in all experiments which means around 75% oxygen excess
- oil concentration in the feedstock: around 26.5 %wt oil-in-water emulsion in all experiments which mean an initial COD entering the reactor around 98 g/l.

Figure 2 shows the temperature profiles obtained along the tubular reactor in experiments carried out with the value for operating parameter mentioned. All experiments were carried out at constant pressure of 250 bar. As can be observed, an increase of 10 degrees in the temperature of water stream before mixing with the oil stream involves a significant increase in the profiles along reactor which mean that the reaction take place at a higher rate, an important conversion of the oil takes place in the firsts meters of the reactor and then major of the heat of reaction is also generated in that first part of the reactor. Taking into account that the reactor is isolated (although not adiabatic), this fact involves a higher increase of temperature. The heating capacity of the effluent of the reactor at higher temperature is used in the heat exchangers to preheat both water stream and air stream before they were mixing at the beginning of the reactor. This way, the electric power needed in the electrical preheater of the water stream is much lower, reducing the operating cost of the treatment. However, although heat utilisation had been carried out, the system did not operate auto-thermally in those experiments and the electrical preheater was also needed.

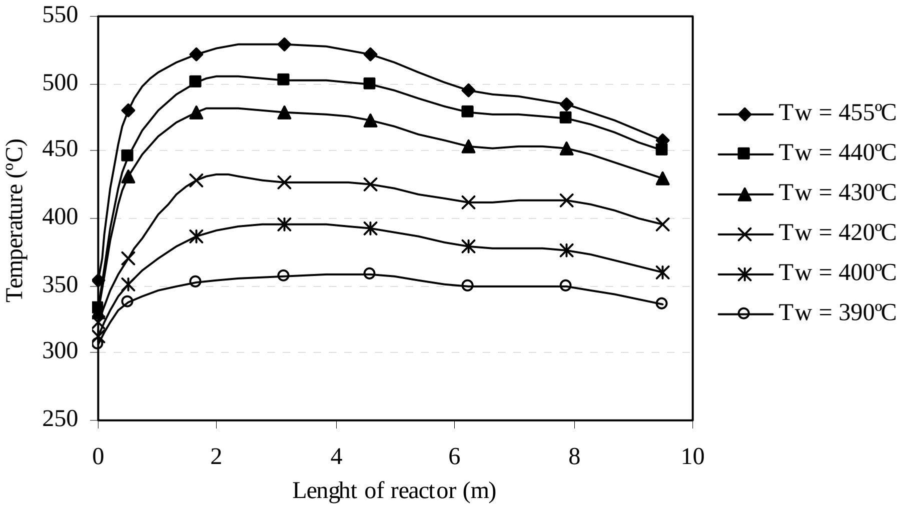

Figure 2: Temperature profiles along the reactor in SCWO experiments of cutting oils at different initial temperature for water stream.

Table 1 shows the operating conditions and the results obtained in experiments. As can be observed an average temperature along the reactor has been calculated for each experiment from the corresponding temperature profiles. Although the same flowrates have been employed in the experiments different residence times have been have resulted consequently with these different temperature profiles.

Experiment nº	1	2	3	4	5	6
Flow rate of cutting oil (kg/h)	2.00	1.99	1.97	2.01	1.99	1.98
Flow rate for water (kg/h)	11.86	11.94	12.11	11.79	11.68	11.69
Flow rate for air (g/min)	196	194	196	185	184	194
Final Temperature of water in electrical preheater, Tw (ºC)	390	400	420	430	440	455
Initial COD in mixture point of three streams (g O_2/l) (referred at room temperature)	97.94	97.08	96.07	99.64	99.90	98.02
Initial temperature in mixture point (ºC)	310	312	323	330	334	354
Average Temperature (ºC)	352	377	410	457	479	499
Residence time (s)	1.1	0.82	0.62	0.58	0.58	0.55
%COD conversion	83.3	86.4	88.2	94.0	96.1	97.5

Table 1: Operating conditions and results obtained in the SCWO pilot plant of cutting oil

The effect of temperature over %COD conversion has been also stated. As can be seen in figure 3, there is a clear effect of temperature over the percentages of COD removal obtained: at higher temperature, higher COD conversion is obtained even also residence time decrease.

In all cases greater than 80% COD conversion is obtained, getting a maximum conversion of 97.5% with 0.55 min of residence time at 500 ºC of average temperature.

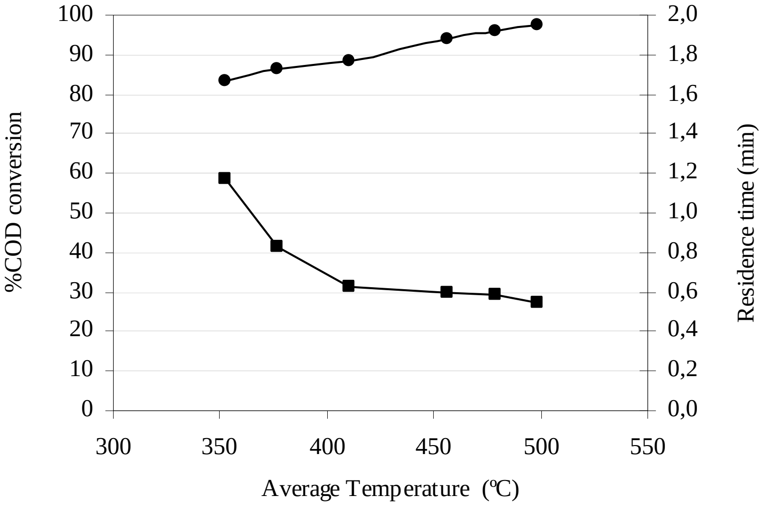

Figure 3: Residence time and % COD conversion in SCWO experiments of cutting oils at different initial temperature for water.

CONCLUSION

The pilot plant facility developed in Univesity of Cádiz has been applied successfully to treat by SCWO a high concentrated oily stream using the direct injection of this stream just before entering the reactor where it is mixed with the supercritical water stream that dissolves completely the oily compounds, obtaining a high % COD conversion in the process. Different temperature profiles have been obtaining depending on the operating conditions employed which mean that it is possible to control the process leading to both safe and efficient performance of the process. Utilisation of the heating capacity of the effluent of the reactor in the heat exchangers to preheat both water stream and air stream allowed an important reduction of the electric power of water stream electrical preheater, reducing the operating cost of the treatment. However, although heat utilisation had been carried out, the system did not operate auto-thermally in operating conditions studied. More experiments are needed in order to establish the best operating condition to achieve the system can operate auto-thermally. The system and procedure included in this work is under patent [2].

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