

COMPARISON OF DIFFERENT HYDROTHERMAL PROCESSES FOR THE ELIMINATION OF CUTTING FLUIDS WASTES

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Cutting fluids are widely used in metalworking industries for lubrication, cooling and removal of metal filings. Under most current legislations, used cutting fluids are considered hazardous wastes and conventional treatment methods are often environmentally unacceptable. In this work we evaluate the application of different technologies based on hydrothermal treatment.

The hydrothermal processes, that is, those that use high pressure and temperature water as reaction medium, have demonstrated a great potential and effectiveness for the treatment of industrial wastewaters with high organic concentration. The aim of this work is to compare the suitability of wet air oxidation, supercritical water oxidation and hydrothermal gasification (sub- and supercritical) applied to the treatment of cutting fluid wastes.

With these technologies, besides the complete purification of these wastewaters, it would be possible to carry out the use of their energy potential: with the process oxidation processes by recovering the combustion heat released (since oxidation reactions are strongly exothermic); with the gasification, by burning the gas effluent generated (of great heating power due to its high content in hydrogen and slight hydrocarbons). This work describes the results obtained both at laboratory and pilot plant scale. From the results obtained at laboratory scale, supercritical water oxidation was selected as the best process and cutting oil wastes were treated at pilot plant scale by using a new patented system suitable to treat non water-soluble wastes. This paper studies the best procedure and operating conditions to mix 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.

1. INTRODUCTION

Cutting fluids are widely used in metalworking industries for lubrication, refrigeration and evacuation of filings. Its composition is variable depending on the requirement of the mechanical process in which it is used. The main components present in cutting fluids are: refrigerant (water), lubricants (mineral oils, vegetal oils, synthetic oils), tensioactives (anionics, non ionics), inhibitors for corrosion (amines, borates, nitrites...), humectants/stabilizers, biocides, additives of high pressure and antifoaming compounds. Depending on the relative percentages of refrigerant, lubricant and additives, the cutting fluids can be classified in different types: synthetics, semi-synthetics and cutting oils, being the semi-synthetic one the most used. After a long use, the cutting fluids lose their properties and accumulate physical and chemical contaminants, so they must be replaced (Burke, 1991). Under most of current legislations, used cutting fluids are considered hazardous wastes and its safe collection and disposal must be ensured. Conventional treatment methods for oily wastes disposal include evaporation, phase-separation and filtration. Those methods are often environmentally unacceptable, since they are not destructive and generate a lower volume of concentrated waste that is always more hazardous than the original one. In other words, non destructive treatments of these wastes are not satisfactory

because of the generation of a sludge which does not fulfill the current legislation. Another possibility to eliminate these wastes is incineration, being in many cases environmentally unacceptable. In this way, the development and application of new destructive technologies is highly necessary. The treatment of oily wastes by hydrothermal processes could be an interesting alternative to conventional methods since they may produce energy, being effective and environmentally clean technologies.

Wet Air Oxidation (WAO) and Supercritical Water Oxidation (SCWO) are two forms of hydrothermal oxidation that have been proved to be effective processes to treat a wide variety of industrial wastes, but hardly tested for oily wastes.

WAO is typically operated at temperatures and pressures ranging from 200 °C to 330 °C and from 2 MPa to 20 MPa, respectively (Mishra et al, 1995). WAO was first developed and applied as a commercial process by Zimmerman (1958), being a commercially available technology useful to eliminate a wide range of problematic wastes from a wide variety of chemical industries especially when those wastes are too dilute to incinerate and too toxic to biotreat. Reaction times in the WAO process are normally up to several hours, and a complete destruction of the organic material is not always achieved, so a further waste treatment may be necessary.

SCWO is carried out at pressures and temperatures above the critical point for pure water, usually ranging from 400°C to 650 °C and from 25 MPa to 35 MPa, respectively (Bruner, 2008). The SCWO process is based on the special physical properties of supercritical water. When exceeding its critical point, the values of density, dielectric constant, and ionic product of water drop down, acting as a non-polar solvent of high diffusivity and excellent transport properties. Consequently, organic compounds and gases like oxygen become completely miscible with supercritical water.

As a result of these properties and the extreme operating conditions, considerable reaction rates are experienced with the subsequent reduction of residence times. The reaction end products are mostly CO₂ and simple acids so the treated effluent may be dumped into the public sewage with no need of further post-treatment. SCWO is a promising emerging technology that has been widely tested both at laboratory and pilot plant scales, but it is not yet fully established as a commercial process.

In the case of refractory wastes, WAO process is not efficient enough due to the moderate temperatures used. SCWO is a more powerful process since operating temperatures are usually around 600 °C.

Among the hydrothermal processes it is possible to highlight Supercritical Water Gasification (SCWG), a process that occurs in the partial or total absence of dissolved oxygen. In SCWG the water contained in wastewaters is used as a solvent as well as a reactant, meaning that a drying procedure is not required for gasification (Basu & Mettanant, 2009). In this work, SCWG has been applied to cutting oils, that contain a high concentration of organics and have a high energy potential. In this way, besides the purification of the industrial wastewater, it is sought to harness their energy potential by using the gas effluent generated in the hydrothermal gasification – a gas that should have great heating power due to its high content in hydrogen and light hydrocarbons. Hydrogen is an obvious alternative to hydrocarbon fuels. This gas has many potential uses, it is safe to manufacture and it is environmentally friendly. Hydrogen is expected to play a key role in the world's energy future by replacing fossil fuels and, as such, it is gaining increasing attention as an encouraging future energy source (Hao et al, 2003). In this way, SCWG is a promising technology as an application for producing fuel from organic resources (García-Jarana et al, 2008).

Gasification of glucose in supercritical water has been studied as a good model for the gasification of more complex wastewaters. The composition of the gas phase produced consisted mainly of carbon dioxide, hydrogen and carbon monoxide, along with small amounts of methane and gases with two carbons (Williams & Onwudili, 2005). In the case of real wastewaters (Herguido et al, 1995), not all of the organic molecules are transformed into hydrogen or carbon dioxide. As a result, tars and chars can be formed during the supercritical water gasification. As a result of sedimentation, these chars and tars usually plug reactors after several hours of running. Moreover, they limit the amount of hydrogen formed. Chars come from non-converted organics, while tars are unwanted reaction products, usually formed by pyrolysis of organic molecules. The amounts of these materials can be effectively reduced by the use of a catalyst in the SCWG process to obtain high

conversion yields. For example, Schmieder et al. (2007) showed that the addition of KOH increases the production of H_2 .

This work studies WAO, SCWO and hydrothermal gasification (sub- and supercritical) applied to the treatment of cutting fluid wastes. The aim of this work is to compare the suitability of those technologies, searching both the complete purification of these wastewaters and the use of their energy potential: with the process oxidation processes by recovering the combustion heat released (since oxidation reactions are strongly exothermic); with the gasification, producing H_2 or by burning the gas effluent generated.

2. EXPERIMENTAL

2.1 Description of the continuous flow reactor

The flow reactor operated both at sub- and supercritical conditions. Figure 1 shows a schematic diagram of the laboratory-scale, continuous flow reactor system. All wetted parts, from the pumps to the back-pressure regulator, were made of stainless steel 316. The reactor was constructed from a 2.5m length of 1/4 in.-o.d. tubing. The oxidant feed stream was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank equipped with a magnetic stirrer was loaded with an aqueous solution of glucose. All H_2O_2 is decomposed to give H_2O and O_2 in the preheating systems.

After preheating, the two lines were mixed at the reactor inlet. Upon exiting the reactor, the effluent was cooled rapidly in a counter current heat exchanger and afterwards, the system pressure was reduced by using a back-pressure regulator. The product stream was then separated into liquid and vapor phases. More specific details of the experimental apparatus and procedure are well described in our previous studies (García-Jarana et al., 2008).

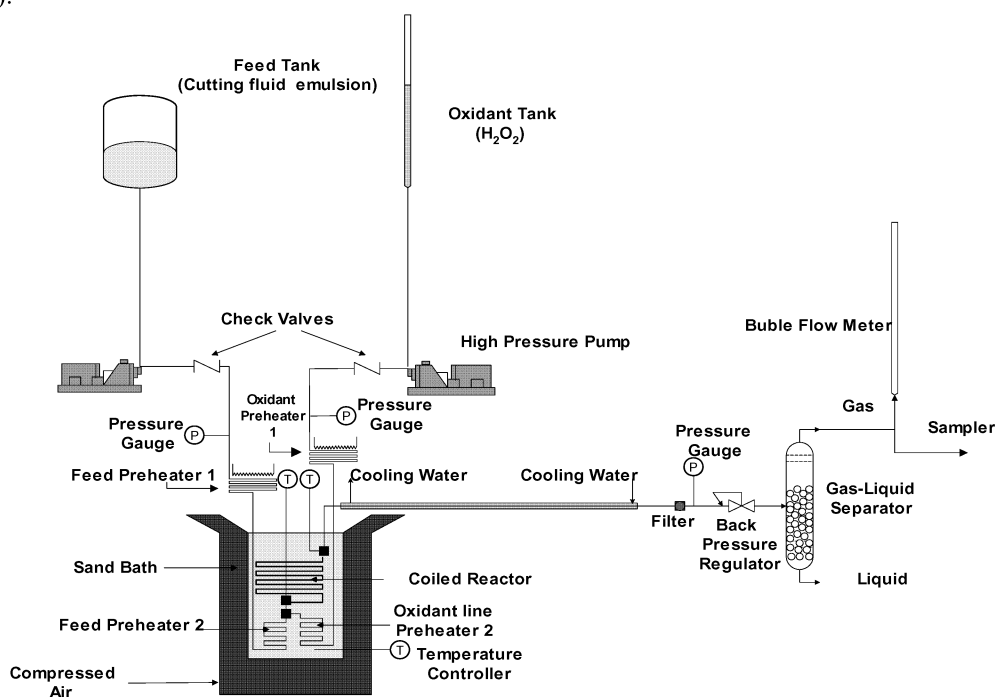


Figure 1. Schematic diagram of the continuous flow reactor system

2.2 Description of the pilot plant

At pilot scale, supercritical water oxidation experiments were conducted in the SCWO UCA pilot plant facility. A schematic diagram is shown in Figure 2. This pilot plant includes three independent feed streams:

- 1) An aqueous feed stream (in this experiments we use clean water) is pressurized by a high pressure liquid pump, preheated at supercritical temperature (above 400°C) 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 (an oil waste in this work). 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. All parameters can be registered and controlled by SCADA software. The system and procedure included in this work is under patent (Portela et al, 2007).

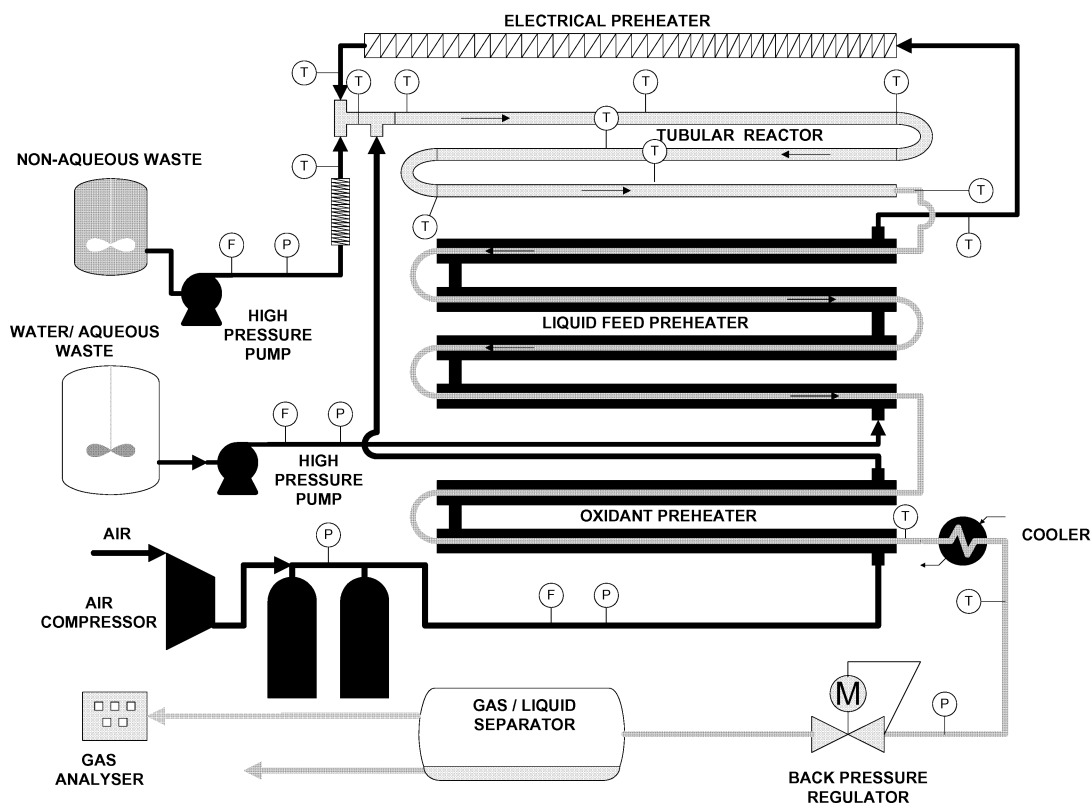


Figure 2. Schematic diagram of the patented system for SCWO

2.3 Materials and analytical methods

The cutting fluid studied in this work are semi-synthetic type. It has been chosen because of they are the most used in the industry studied (Delphi Automotive Systems). The formulation of concentrated semi-synthetic cutting fluid normally contains between 20 – 50% water, 10 – 40% mineral or synthetic oils, 10 – 30% tensioactives and 10 – 30% additives. The concentrated cutting fluid is diluted “in situ” with deionized water, normally between 2 – 6% v/v in the metalworking industry. The main properties of cutting fluid waste from metalworking industry (with confidence limits of 95%) are pH= 8.6 ± 0.2 , Conductivity= 3.5 ± 0.9 (mS•cm⁻¹) and COD= 160 ± 30 (g•l⁻¹).

COD was analyzed by closed reflux colorimetric method. Gas samples were analyzed using an HP 6890 Series gas chromatograph with a Thermal Conductivity Detector (TCD). Two in-series columns were used to separate CO from CO₂. A temperature ramp from 55 to 160 °C (at 15 °C/min) was used. The system was calibrated with a standard gas mixture containing H₂, O₂, N₂, CO₂, CO and CH₄. More details of the experimental section has been described by Portela et al (2001).

3. RESULTS AND DISCUSSION

3.1 Hydrothermal oxidation at laboratory scale

The efficiency of COD removal was clearly enhanced by the temperature. In this way, hydrothermal oxidation at subcritical conditions is not powerful enough to destroy those wastes, but it is possible to completely reduce the COD content at supercritical conditions. As can be seen in figure 3, at 300°C below 40% of TOC removal was obtained in 40 s. At 350 °C it is possible to reach a 70% of COD removal, but it would be necessary a post-treatment to completely eliminate the COD present in the wastewater. However, at 500 C and only 9 seconds of residence time these percentages of elimination were increased to around 98% of COD. These good results obtained from oxidation experiments show that SCWO is a powerful technology suitable for the elimination of cutting oils wastes.

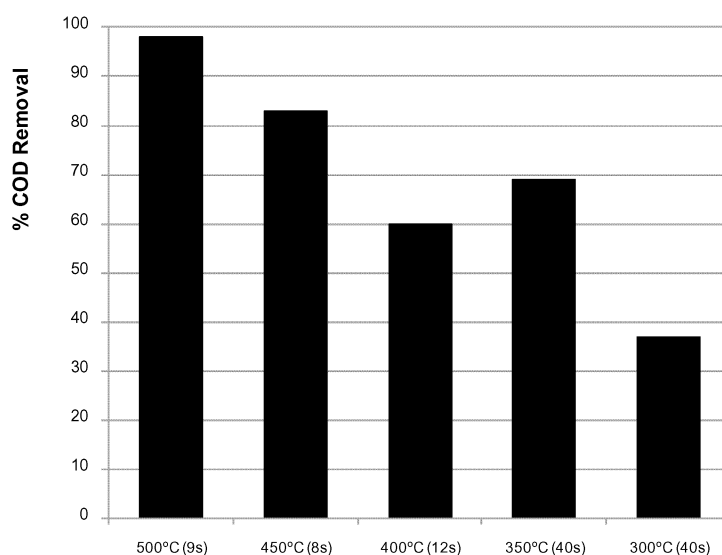


Figure 3. COD elimination for hydrothermal oxidation of the cutting oil

3.2 Hydrothermal gasification at laboratory scale

Hydrothermal gasification process in subcritical conditions ($T < 374$ °C), is not suitable to produce a fuel gas and higher temperatures are needed to generate H_2 and CH_4 from cutting oils.

The efficiency of the hydrothermal gasification process in supercritical conditions (SCWG) was followed in terms of the reduction in chemical oxygen demand (COD) and the composition of the gas phase generated (H_2 , CH_4 , CO_2 , and CO). All experiments were carried out at 450 °C and 250 bar and the initial concentration of the wastes was around 12 g/l. In this study the main operation variables were the addition of oxidant and catalyst. Half of the experiments were carried out in total absence of oxygen ($n=0$) and the rest with 10% of the stoichiometric oxygen ($n=0.1$). Experimental conditions are presented in Table 1.

Table 1. Summary of operating conditions for SCWG experiments.
(*) n = Oxygen/Stoichiometric Oxygen. ($n=1$ means initial oxygen corresponding to stoichiometric)

Waste	Temperature (°C)	Residence time (s)	Oxygen coefficient (n) *	Catalyst
Cutting Oil	450	17	0	-
	450	19	0.1	-
	450	17	0	KOH (4×10^{-3} M)
	450	18	0.1	KOH (4×10^{-3} M)

As can be seen in figure 4, experimental results for COD disappearance show that a maximum of 10-20% of COD removal is possible with SCWG, and the best results were obtained at conditions of $n=0.1$ and absence of catalyst.

The best composition of gas phase generated in the experiment were obtained at conditions of $n=0.1$ and presence of KOH because H_2 is formed greater amount. Even though it is possible to obtain more than 30% of H_2 in the gaseous product, the flow rate of gas is very low and the molar yield is insignificant (1.5 moles of s moles of H_2 per kg of initial COD).

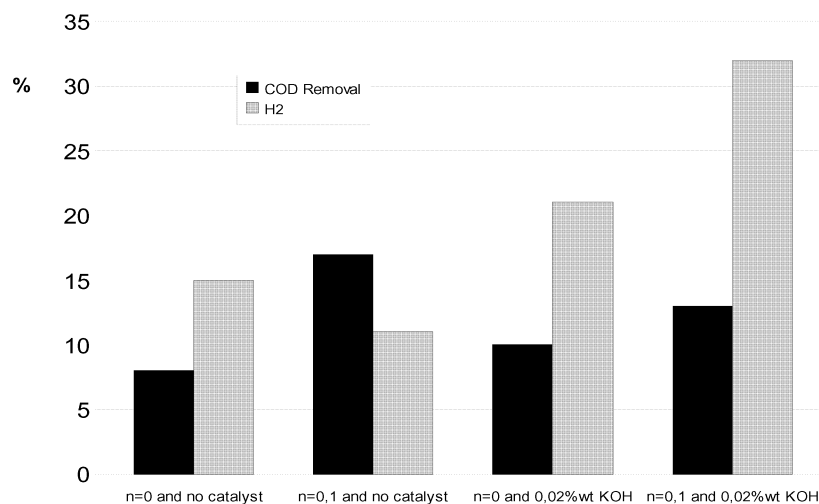


Figure 4. COD removal (%) in the liquid phase and hydrogen (%) produced in the gaseous phase. All experiments were carried out at 450 °C and 250 bar, and the initial concentration of the wastes expressed as COD was around 12 g O_2/l .

The effect of reaction temperature on the gasification process was studied maintaining the conditions selected ($n=0.1$ and presence of KOH) and temperatures of 500 and 550°C). Figure 5 shows the results obtained. In terms of COD removal, it is possible to clearly improve the yield at 550 °C, where 80% COD removal is obtained. However the H₂ yield is still too low to justify SCWG process as an alternative to conventional methods.

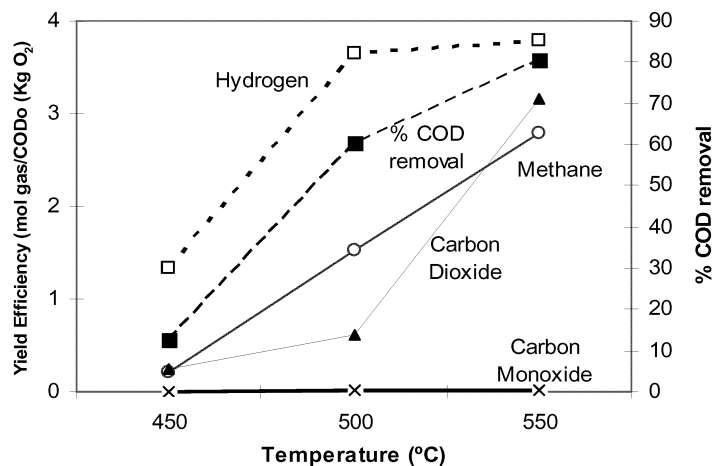


Figure 5. Effect of temperature on the composition of gaseous phase and %COD removal from cutting oil gasification at 250 bar, $COD_o=12 \text{ g O}_2/l$, $n=0.1$ and presence of catalyst ($[KOH] = 4 \times 10^{-3} \text{ M}$).

From the results obtained for SCWG at laboratory scale, supercritical water oxidation was selected as the best process and cutting oil wastes were treated at pilot plant scale

3.3 Supercritical water oxidation at pilot plant scale

The pilot plant facility developed in University of Cádiz has been applied successfully to treat the cutting fluid waste by 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. Figure 6 shows an experiment where the heat of effluent can be used to preheat the feed without using the electrical heaters. That is, it has been proved that if the reactor feed is concentrated enough, it is possible to obtain 98.5 % COD removal and to generate the energy required to work under autothermal operation. It is important to point out that the tubular reactor is thermally isolated, but it is not adiabatic, so the system loose an important part of the energy released in the reactions.

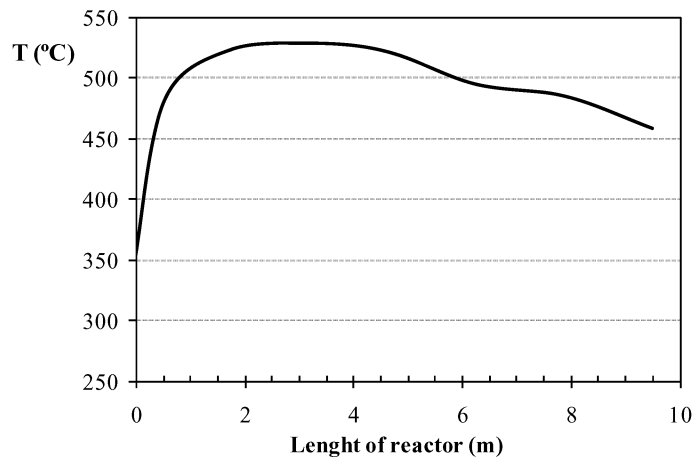


Figure 6. Temperature profile along the reactor in a experiment carried out with initial COD around 12 g O₂/l

Besides, it has been demonstrated that it is possible to obtain similar results but avoiding to preheat the feed containing organics. In this way, two different experiments were carried out: 1) in one experiment both liquid feed streams were preheated, but only at 200°C for the oil waste, in order to reduce the possible hydrolysis/pyrolysis reactions. The conversion is high (96.4%) and the system worked autothermally. 2) A similar experiment was carried out, but without preheating the high concentration feed (so, in order to obtain the same temperature after mixing both liquid feed streams the water feed must be preheated to a higher temperature), being possible to obtain a similar temperature profile and conversion (98%), avoiding to preheat the organics.

3.4 Effect of the feed flowrates on the reactor temperature profiles

Figure 7 shows several experiments that were carried out reducing progressively the flowrate of the oil waste feed, producing a dilution at the reactor inlet from 110 to 30 g/L. This set of experiments demonstrates that the temperature profile along the reactor can be easily modified by adjusting the feed streams flowrates. That is, if the concentration is so high that the plant is under risk, the control system just reduces the flowrate of the oil waste feed, being possible to let's say “turn off” the reactor really fast, but the whole system remain stable “pumps, flowrate, pressure, preheaters, etc”. In other words, it is possible to easily correct the system and continue working.

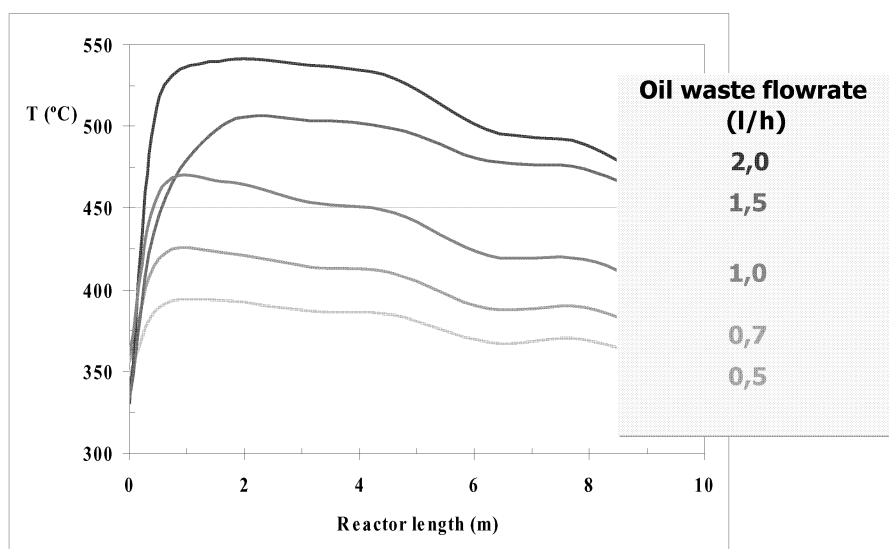


Figure 7. Effect of the feed flowrates on the reactor temperature profiles

4. CONCLUSIONS

Hydrothermal processes of oxidation and gasification of cutting oil have been tested at laboratory scale for both subcritical and supercritical conditions. Hydrothermal oxidation at subcritical conditions is not powerful enough to destroy those wastes, but it is possible to completely reduce the COD content at supercritical conditions. Hydrothermal gasification process in subcritical conditions is not suitable to generate H_2 and CH_4 from cutting oils. At supercritical conditions, it is possible to obtain more than 30% of H_2 in the gas phase, but both the gas flow rate and the molar yield of hydrogen are very low.

The pilot plant facility developed in University 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 obtained 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. The major advantages of the innovation presented are:

- Treatment of water-insoluble residues
- Wider range of wastewaters to be treated in a SCWO system (from diluted to pure)
- No need of preheating (no pyrolysis/hydrolysis)
- Better control (on-line concentration adjustment)
- More safety (no need to stop the whole plant)

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