

Comparison of different hydrothermal processes for the elimination of cutting fluids wastes

Juan R. Portela*, J. Sánchez-Oneto, M. B. García-Jarana, E. Nebot Sanz, E. J. Martínez de la Ossa

Department of Chemical Engineering, Food Technology and Environmental Technologies. University of Cádiz
Faculty of Sciences. 11510 Puerto Real (Cádiz), Spain.

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).

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. Since conventional treatment methods (evaporation, phase separation, filtration) are often inefficient or environmentally unacceptable, the development and application of new technologies is highly necessary.

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. 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 (Tester et al, 1993; Mishra et al, 1995),

Supercritical water gasification (SCWG), is a promising technology in which supercritical water is not only a solvent for organic materials but also a reactant, being one of the applications for producing fuel from organic resources (García-Jarana et al, 2008).

This work is 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 H₂ or by burning the gas effluent generated.

2. Experimental

2.1 Description of the batch reactor

The batch reactor, only used in the subcritical range, was a 316 stainless steel reactor (Autoclave Engineers) with a capacity of 300mL. The vessel was fitted with a variable-speed stirrer (MagneDrive) and an electric furnace. A constant temperature was maintained at ± 2 °C from the set point by means of an electronic controller (PID). The experimental system incorporated a rupture disk with a burst pressure of 20 Mpa as a safety device in case of pressure buildup in the reactor during an experiment. Figure 1 shows a schematic drawing of this apparatus used in this work.

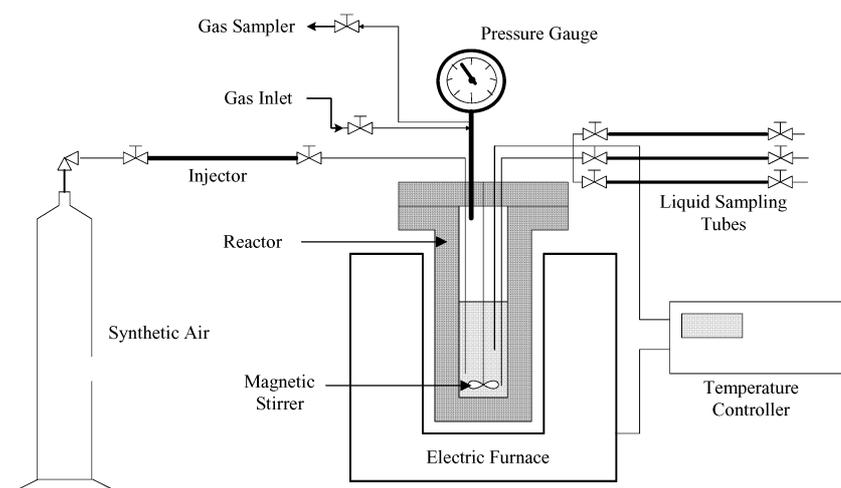


Figure 1. Schematic diagram of the wet air oxidation reactor system

The reactor was charged with initial volume of the waste, pressurised with air or nitrogen and the system was heated to the desired temperature for each experiment and the stirrer speed was adjusted to 7.5rev/s. The zero time for the reaction was taken when the temperature set point had been reached. The reaction temperature and pressure were maintained during the course of the experiment. At the end of each experiment, when room temperature had been reached, gas effluent was depressurized slowly and passed through the gas sampler. A single gas sample was taken and analyzed by gas chromatography in order to determine the gas product composition.

2.2 Description of the continuous flow reactor

The flow reactor operated both at sub- and supercritical conditions. Fig. 2 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.

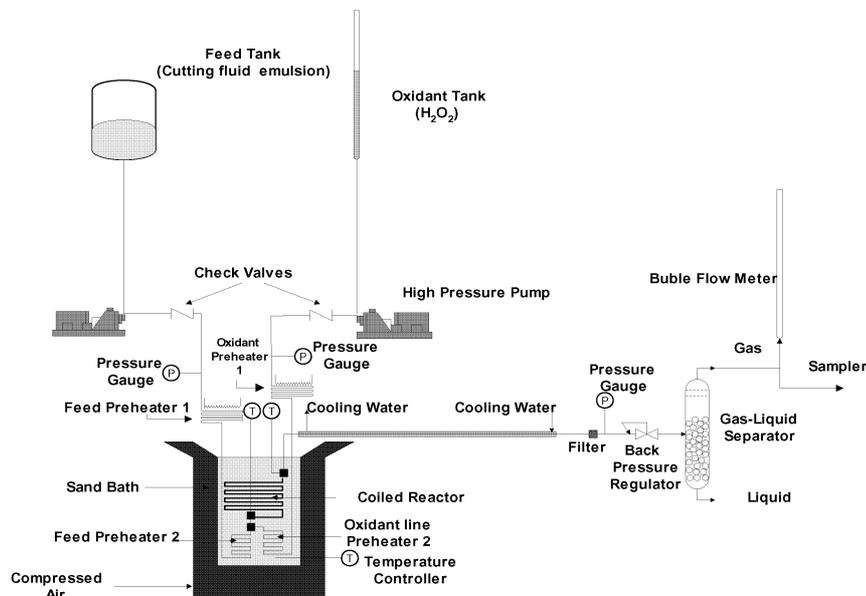


Figure 2. Schematic diagram of the continuous flow reactor system

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 $\text{pH} = 8.6 \pm 0.2$, $\text{Conductivity} = 3.5 \pm 0.9 \text{ (mS}\cdot\text{cm}^{-1}\text{)}$ and $\text{COD} = 160 \pm 30 \text{ (g}\cdot\text{l}^{-1}\text{)}$. 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. More details of the experimental section has been described by Portela et al (2001).

3. Results and discussion

3.1 Hydrothermal oxidation

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.

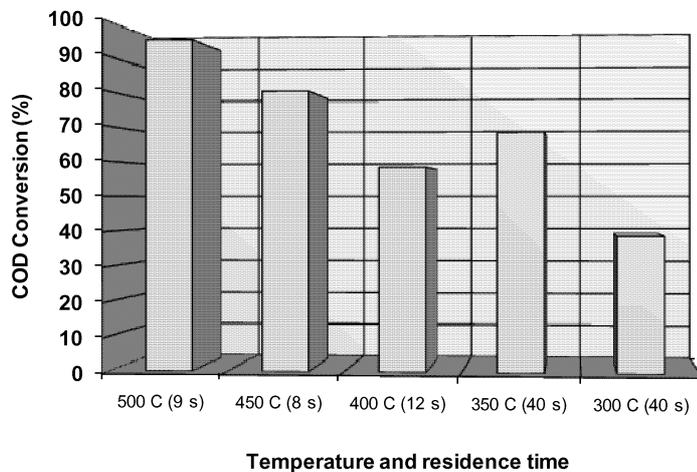


Figure 3. COD elimination for hydrothermal oxidation of the cutting oil

3.2 Hydrothermal gasification

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. When the quantity of initial oxygen is corresponding with stoichiometric $n=1$

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

Experimental results for COD disappearance show that a maximum of 20-30% of COD removal is possible with SCWG at the conditions studied. 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.

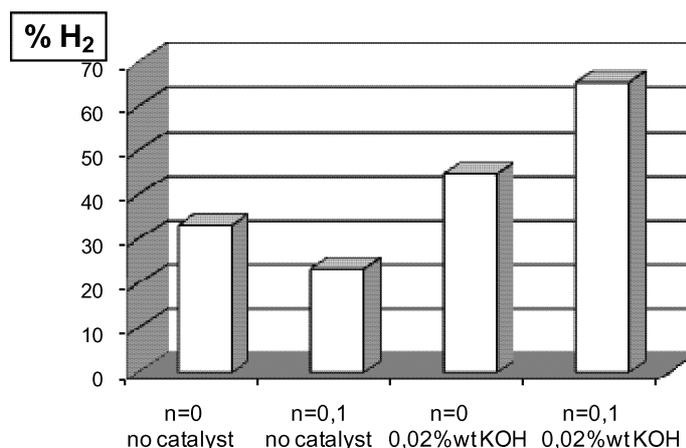


Figure 3. Hydrogen present in the gaseous phase at different conditions.

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 up to 70% of H_2 in the gas phase, but COD reduction is below 30 %.

References

- Burke, J.M. 1991, Waste treatment of metalworking fluids, a comparison of three common methods, *Lubrication Engineering*, 47 (4) 238.
- García-Jarana, B.; Sánchez-Oneto, J.; Portela, Juan R.; Nebot, E.; Martínez de la Ossa, E., 2008. Supercritical Water Gasification of Industrial Organic Wastes. *Journal of Supercritical Fluids*, 46, 329-334.
- Mishra, V.S., V.V. Mahajani; J. B. Joshi, 1995. Wet air oxidation, *Ind. Eng. Chem. Res.*, 36, 2.
- Portela, J. R., Nebot, E., Martínez de la Ossa, E. 2001. Generalized kinetic models for supercritical water oxidation of cutting oil wastes, *J. Supercrit. Fluids*, 21, 135-145.
- Tester, H.R. Holgate, F.J. Armellini, P.A. Webley, W.R. Kililea, G.T. Hong, H.E. Barnern, 1993. Supercritical water oxidation technology. Process development and fundamental research, *ACS Symp. Ser.* 518, 35-76.