WASTEWATERS TREATMENT OF OLIVE OIL INDUSTRY BY HYDROTHERMAL OXIDATION

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Introduction

The production of olive oil are concentrated in the countries around the Mediterranean see: Espagne, Portugal, Italia, Greece, Torque, Tunisia and Marco. These countries represent more that 90% of the world production. The wastewaters issue to olive oil industry are charged out of polluting matters which produce a negative impact on the natural medium and especially the reserves of water and the production of drinking water.

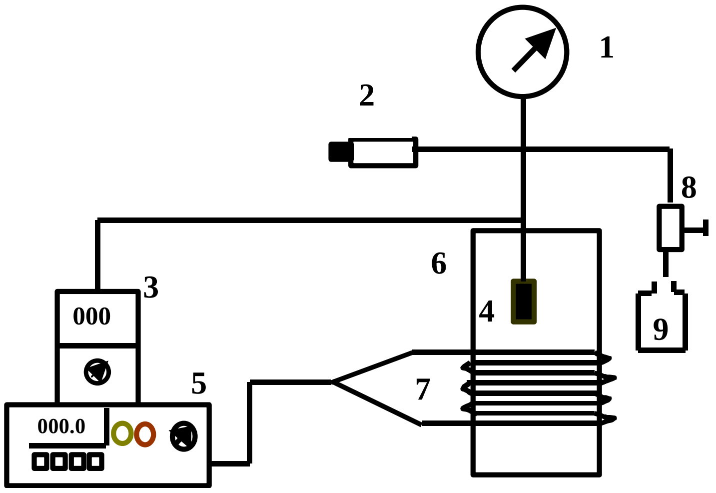
The wastewaters of olive oil industry are obtained after triturating of olives [1]. These wastewaters are black colouring (brown dark), odorous liquids and characterized by the presence of a large quantity of polyphenols. These wastewaters contain 7 to 15% of organic matter in weight %. This fraction is primarily made up of glucids, proteins, vitamins, phenolic compounds and polyphenols. These wastewaters contain also mineral fraction around 2% of the dry matter. This mineral fraction is primarily made up of phosphates, chlorides, sulphates, calcium, magnesium and potassium. The biological oxygen demand (DBO5) and the chemical oxygen demand (COD) are ,according to the method of triturating, up to 60 g/l and 160g/l respectively [2].The pH of these wastewaters is close to 5.

Several methods of treatment, such as biological treatments, coupled or not with a physical pre-treatment, was developed [3,4]. Treatment of wastewaters from olive oil industry was already performed by hydrothermal oxidation [5,6]. Hydrothermal oxidation combines pressure and temperature like activators of reaction [7]. The hydrothermal oxidation process leads to non-toxic end product [8-10]. The organic matter (CHO) is converted in CO_2 and H_2O exclusively.

In this work, wastewater from olive oil industry was treated with a batch reactor up to 550°C and 25 MPa. The determination of optimum operating parameters, which permit a total destruction of organic matters of wastewaters and so removing of the out put effluent to natural media, will be presented.

Experimental set-up

Fig. 1 shows a schematic diagram of the pilot plant facility developed in our laboratory. This pilot plant facility is able to treat in batch reactor aqueous wastes in a temperature range of 50 to 600 °C at pressures up to 30 MPa.



(1) Pressure sensor;
(2) Rupture disc;
(3) Temperature analyser;
(4) Thermocouple;
(5) Temperature regulator;
(6) Batch reactor (100cm^3);
(7) Heating rolling up;
(8) Back pressure regulation;
(9) Tank for end-products.

Figure 1: Schematic diagram of the pilot plant facility

The reactor is filed at ambient temperature with oxidant and waste in defined quantities which permit, after heating of the reactor until the working temperature, to get the working pressure.

The analysis is based on the evolution of the chemical oxygen demand as function of the operating parameters of the hydrothermal oxidation experiments**.** The chemical oxygen demand is the oxygen concentration, expressed in milligram per litter, which is necessary to transform the organic matter (CHO) in CO_2 and H_2O. At the end of the reaction, the COD measurements are performed on the liquid phase

The selected oxidant is the hydrogen peroxide (solution of H_2O_2 at 35% in weight %). The experiments are carried out at 5 temperatures : 200°C, 300°C, 400°C, 450°C, 500°C, with a stoechiometry in oxygen equal to 0,1 and 2. The residence time for the tests is one hour under the working conditions. The working pressure is in the range of 1.7 to 25 MPa.

Experimental results

Table 1 summarizes the principal results in term of convertion rate on the DCO.

N° exp.	P (MPa)	T (°C)	Stoechiometry in oxygen	DCO Initiale (g/l)	DCO Finale (g/l)	∆DCO en %
1	1.7	205	0	66.7	48.1	27.9
2	5.0	208	1	47.5	15.4	67.6
3	7.4	205	2	36.8	9.1	75.2
4	9.0	300	0	256	40.3	84.3
5	9.0	305	1	99.8	21.1	78.9
6	12	310	2	62.1	4.8	92.3
7	25	408	0	155.1	17.28	88.9
8	25	405	1	99.9	5.4	94.6
10	25	407	2	36.8	5.42	85.3
11	25	453	0	186.2	9.87	94.7
12	25	459	1	74.7	7.6	89.8
13	25	455	2	66.5	3.8	94.2
14	25	510	0	200.9	4.8	95.6
15	25	504	1	72.2	8.7	87.9
16	25	508	2	47.2	2.2	95.4

Table 1: COD reduction of wastewaters from olive oil industry treated by hydrothermal oxidation.

Figure 2 summarizes the COD evolution of wastewaters of the olive oil industry versus temperature and stoechiometry in oxygen. This figure shows, as classically observed, an increasing of COD reduction with temperature and oxygen stoechiometry.
It is important to note that our batch reactor is not a perfect mixed reactor and so it is impossible to get a total reduction of COD. However, the COD reduction, for T=400°C and oxygen stoeckiometry =1, is equal to 94,6 %.

This result is a good information which indicates that with a continuous flow reactor it will be possible to get a COD reduction higher than 99% for T=400°C and oxygen stoeckiometry =1. It is interesting to note that the COD reduction reaches a value close to 70% at a temperature and a stoeckiometry equal respectively to 200°C and 2. So, with the multi-injections system of oxygen, developed at the ICMCB [11], it possible to start the reaction at 200°C.
Figure 3 shows pictures of final effluents obtained after a treatment at 200, 300, 400°C and oxygen stoeckiometry =1. The colour of the recovered samples, which passes from black towards the colourless one, shows well the degradation of the organic matter as function of temperature.

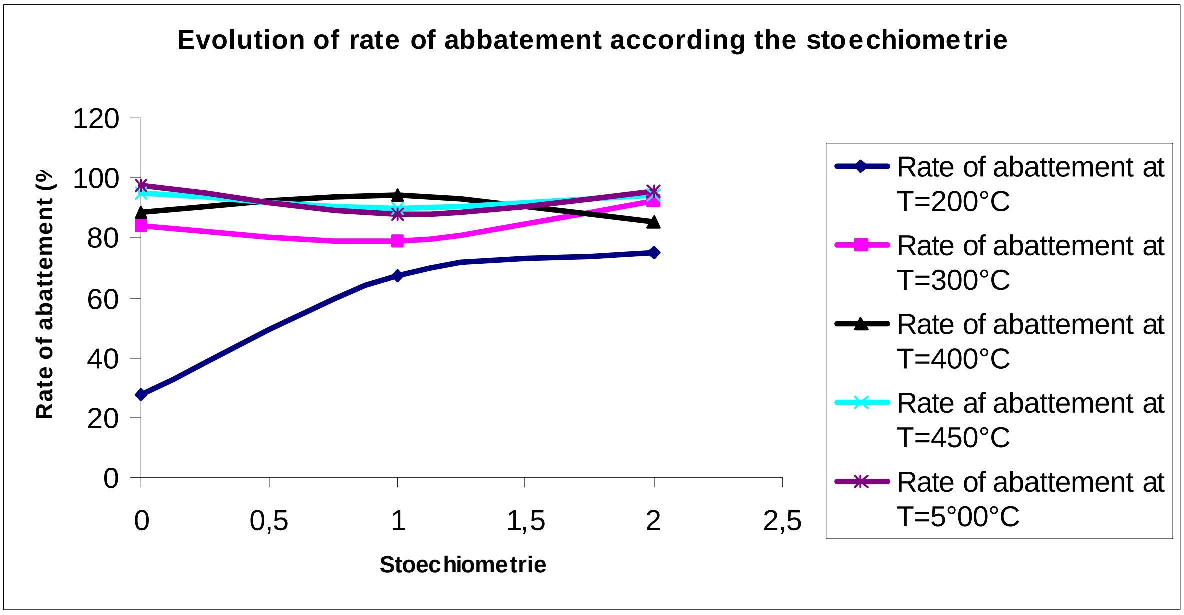


Figure 2: COD reduction of wastewaters of the olive oil industry versus temperature and stoechiometry in oxygen

Figure 3: Final effluents obtain after a treatment at 200, 300 and 400°C, from the left to right respectively

Conclusions

These first results, on wastewaters from olive oil industry treated by hydrothermal oxidation in batch reactor, permit to define the operating conditions which permit a good COD reductions. These operation conditions (T=400°C, P=25 MPa and oxygen stoeckiometry =1) will be used on the ICMCB pilot plant facility. This pilot plant facility is able to treat up to 2.8 $kg.h^{-1}$ aqueous wastes in a temperature range of 200 to 600 °C at pressures up to 30 MPa.

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