

Study of a bubble column for wastewater treatment by wet air oxidation in sub-critical conditions

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ABSTRACT

Wet Air Oxidation (WAO) is a process dedicated to treat liquid effluents by putting them in contact with an oxidizer. The process works in sub-critical conditions: pressure between 0.5 and 30 MPa and temperature between 373 and 593 K. The process is usually carried out in a bubble column where the liquid holdup and the interfacial area are high enough to achieve a high mass transfer.

The lack of available correlations for gas holdup and the mass transfer coefficient k_{La} at high pressures and temperatures, even in clear water, shows the need for experimental investigations in the subcritical region.

In this study, measurement of gas holdup and mass transfer coefficient is carried out inside a pilot-scale bubble column available in the laboratory, 0.04 m inner diameter and 0.84 m high. The pressure effect is studied between 10 and 30 MPa and the temperature effect is studied between 373 and 573 K. The influence of superficial gas and liquid velocities is also investigated. Gas holdup is measured in clear water with nitrogen.

Wet Air Oxidation, Gas Holdup, Bubble Column.

INTRODUCTION

Wet Air Oxidation (WAO) or oxidation in subcritical water is a process dedicated to oxidize the organic fraction of an aqueous effluent or suspension by putting it in contact with an oxidizer (oxygen or air) at temperatures between 423 and 598 K and pressures between 2 and 17.5 MPa. In those conditions, the solubility of oxygen in water is greater than its solubility at ambient conditions, which implies that the kinetic degradation of the organic fraction into CO₂ and H₂O is increased. Usually, the residence time of the effluent varies between a few minutes and several hours. Oxidation yields can be as high as 95%. The organic matter which is not degraded into CO₂ and H₂O is composed mainly of acetic acid, formic acid and other volatile fatty acids. A biological treatment follows the WAO process in order to degrade those compounds, which are totally biodegradable. The exothermic reaction is carried out in a bubble column reactor where the liquid holdup and the interfacial area are high enough to achieve a high mass transfer. At the outlet of the reactor gas and liquid are cooled, depressurized and separated. The gas effluent is purified by a catalytic oxidation in order to eliminate the residual volatile organic compounds and rejected at the atmosphere. The liquid is then treated by a biological installation.

Many studies show the efficiency of WAO in order to eliminate organic pollutants. Nevertheless, few processes have been developed industrially. This work is part of collaboration between the laboratory and the S.A.R.L A³i, which aims to develop a non-

catalytic WAO process that can work at high temperatures and pressures. The absence of catalyst is an important aspect of the process as the presence of a catalyst can increase the operating cost of the process and is not compatible with the long term objective of minimizing matter flows around processes.

Correlations of mass transfer coefficient and gas holdup are needed to optimize and design WAO processes. A bibliographic study (see, among others, [1] and [2]) shows the lack of available correlations and experimental data for the gas holdup at high pressures and temperatures, even in clear water. This study focuses on the measurement of the gas holdup in the subcritical region.

MATERIALS AND METHOD

1. Experimental set-up

Gas holdup is measured in a pilot-scale bubble column, 0.04 inner diameter and 0.84 m high provided by SEPAREX. A simplified diagram of the installation is shown on Figure 1.

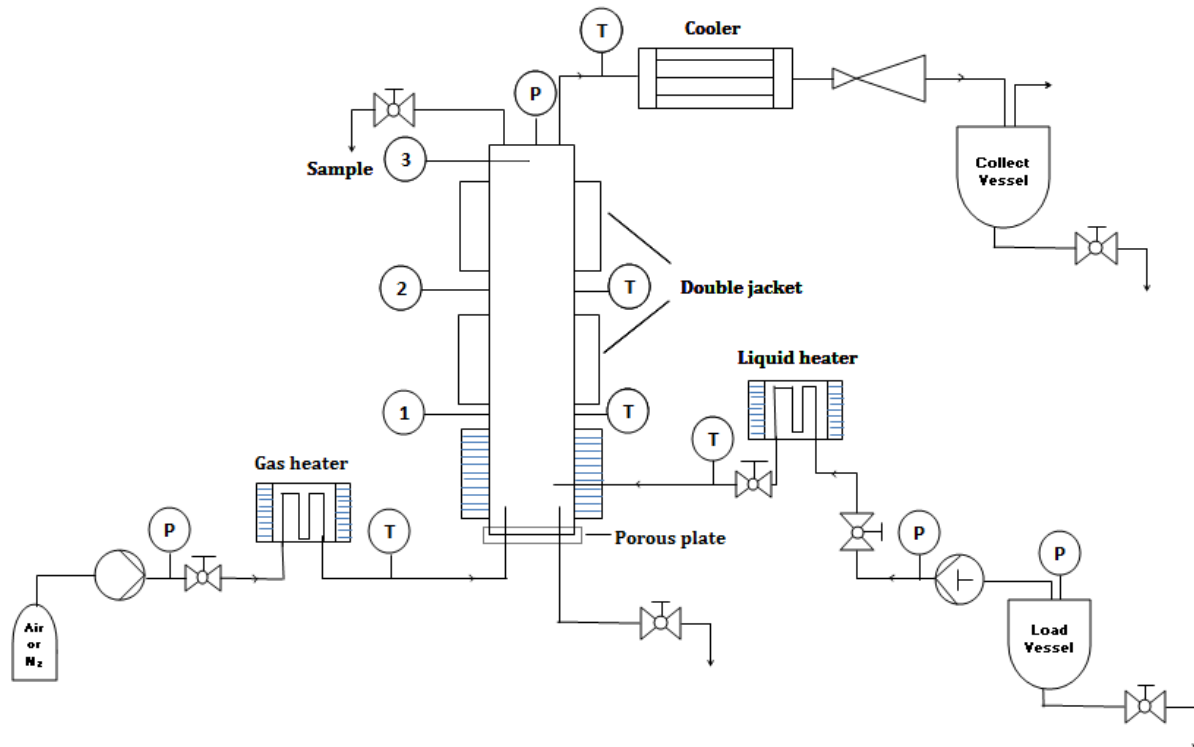


Figure 1 : Simplified diagram of the installation

The column is able to work at pressures up to 30 MPa and temperatures up to 573 K. It is separated into three stages: a first stage is equipped with a heat jacket in order to keep the temperature at the working temperature. The two others are equipped with a double jacket. A cold or a hot fluid can be used in the double jacket: the first one is used to regulate the temperature in presence of a chemical reaction; the other is used without reaction to keep the temperature constant in the column. Three temperatures controllers are used to control and regulate the temperature at each stage. At the bottom of the column, a porous plate (mean pore diameter: 80 μm) is used as a gas sparger.

The gas phase is taken from a high pressure bottle at pressures up to 20 MPa and goes through a high pressure surpressor dedicated to compress it at higher pressures up to 30 MPa.

The gas pump is also equipped with a flow meter placed at the outlet in order to assure a constant flowrate (up to 65 NL.min⁻¹). The gas is then preheated by a gas heater (0.7 m long) at temperatures up to 523 K before entering the column through the porous plate. The liquid phase is first charged into a vessel, pressurized at pressure up to 0.5 MPa, and pumped by a high pressure piston pump with a capacity of 100 g.min⁻¹ before entering a liquid heater able to heat at a temperature up to 573 K. The flowrate is controlled directly by the pump. The liquid is then injected in the column just above the sparger.

A cooler is used at the outlet of the column to cool the gas and liquid phases at ambient temperature. The liquid fall into a vessel where it can be recuperated, the gas phase is rejected at the atmosphere.

2. Materials

For gas holdup measurement distilled water is used. The gas phase, nitrogen, is provided by AIR LIQUIDE (purity > 99%).

3. Operating conditions

Pressure effect is tested between 10 and 30 MPa and temperature effect between 373 and 523 K. Superficial gas velocity can be varied between 0.07 and 1.8 cm.s⁻¹ depending on operating conditions. Superficial liquid velocity is tested between 0 (semi-batch for liquid) and 0.165 cm.s⁻¹. In those conditions, the ratio of gas mass flowrate above liquid mass flowrate is kept between 0 and 2, which is representative of typical industrial conditions.

4. Methods

Gas holdup is measured by the well-known method of measuring differential pressure between two points in the column (see [2]). The column is equipped with three connections (numbered from 1 to 3 on figure 1) that can be used to measure gas holdup in the second stage, in the third stage and in the second and third stages in order to check if the holdup is constant in the column. The differential pressure sensor used in this work is provided by FUJI ELECTRIC and can be operated at pressures up to 42 MPa and temperatures up to 393 K with a precision of ± 3.12 Pa of differential pressure. The sensor is placed at the bottom of the column in order to avoid any accumulation of gas in the tube that connects it to the column. It has been designed to assure that the temperature at the sensor level is the ambient temperature. The pressure difference is read together with the gas flowrate with the help of an acquisition system provided by AOIP.

First the liquid is charged in the column, pressurized at the desired pressure and heated. The gas is then allowed to pass. The presence of the gas increases turbulence and results in an increase of the temperature from T_0 to T_f . Gas holdup is then calculated from the static pressure drop by Equation 1:

$$\varepsilon_G = \frac{\Delta P_m}{g(h_2 - h_1)(\rho_G(T_f) - \rho_L(T_f))} + \frac{\rho_L(T_f) - \rho_L(T_0)}{\rho_G(T_f) - \rho_L(T_f)} \quad (1)$$

The second term is a correction used to take into account the increase in temperature.

This equation is only verified if the densities and superficial velocities are constant between the two points of measurement: pressure losses by acceleration and friction must be

negligible. For our low superficial velocities, calculations were made and show that taking into account the changing in superficial velocity with the saturation of liquid by the gas due to its solubility and the saturation of gas by water vapor lead to negligible pressure losses by acceleration. Pressure losses due to friction were estimated by the Friedel equation for two-phase flows ([3]) and were shown negligible given our low superficial gas and liquid velocities.

RESULTS

1. Influence of superficial velocities

Results show that increasing the superficial gas velocity increases gas holdup, which is consistent with the results obtained at lower pressures and temperatures in the literature (see [2]). Its influence is linear, which proves that the hydrodynamic regime is homogeneous which was expected given our low superficial gas velocities.

An effect of the superficial liquid velocity can be observed. Results for gas holdup are shown on Figure 2, where Q_L is the volumetric liquid flowrate.

Results for $T = 513$ K and $P = 10$ MPa, 2nd and 3rd stages

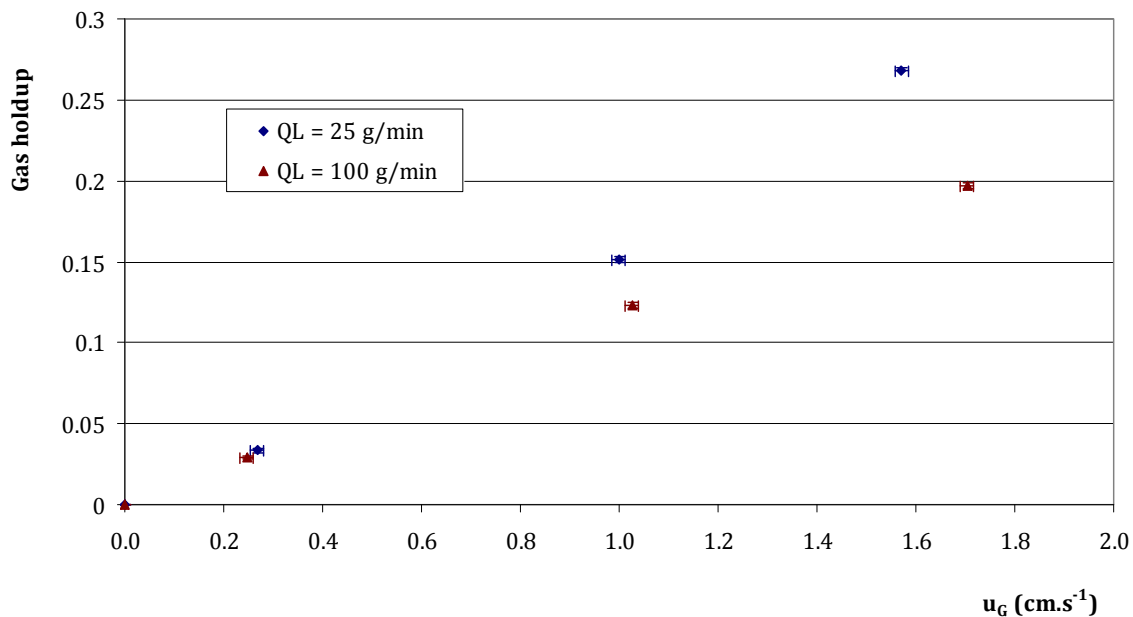


Figure 2 : Gas holdup measurement, effect of superficial velocities.

Its effect is directly related to the effect of evaporation of the liquid and saturation of the gas by the liquid. Indeed evaporation ratio is decreased when increasing pressure and liquid flowrate and decreasing temperatures and gas flowrate. It is clearly observed on Figure 2 that superficial liquid velocity only has an effect at high gas velocities.

2. Influence of pressure and temperature

Pressure influence depends greatly on the temperature conditions and superficial gas velocity. At low superficial gas velocity, no effect can be observed. At higher superficial gas velocity, it seems that increasing pressure decreases gas holdup, as shown on Figure 3.

Results for T = 513 K, 2nd & 3rd stages

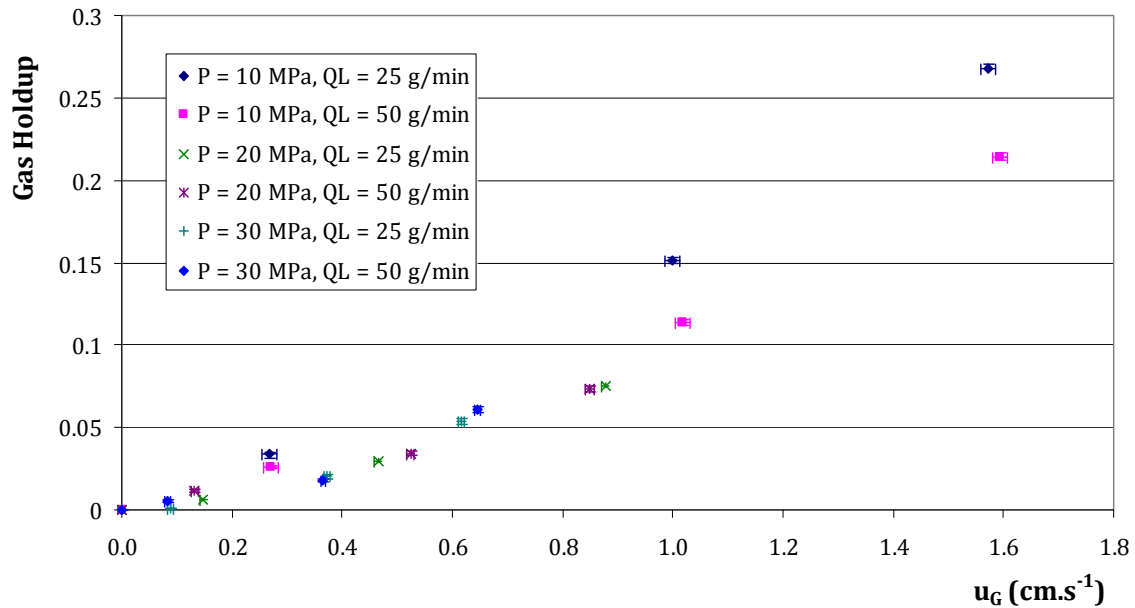


Figure 3 : Gas holdup measurements, effect of pressure at T = 513 K

In fact, this effect can be attributed to evaporation. When this effect can be neglected, typically above 20 MPa, it seems that pressure has no effect. This is consistent with the tendencies observed in the literature for the homogeneous regime [4].

CONCLUSION

It has been shown that the tendencies observed are consistent with some results in the literature. Superficial gas velocity, saturation of gas by vapour and temperature are the main factors that govern the flow in bubble column at subcritical conditions.

This work is not yet achieved and further investigation will be made by measuring bubble diameter in order to calculate the interfacial area and the mass transfer coefficient k_L separately. In the end, correlations of gas holdup, interfacial area, bubble diameter, k_L and $k_L a$ will be proposed.

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