ENERGETIC OPTIMIZATION OF WET AIR OXIDATION PROCESS BASED ON THE PRELIMINARY STUDY ON LIQUID-VAPOR EQUILIBRIUMS.

Sébastien Lefèvre[1,2], Jean-Henri Ferrasse[1], Rémy Faucherand[2], Alain Viand[2], Olivier Boutin[1*]

1 - Aix Marseille Universités, Laboratoire M2P2 UMR CNRS 6181, Europôle de l'Arbois, BP80 13545 Aix en Provence Cedex 4, France

2 - A3i Parc de la Chocolaterie 26290 Donzère

*Phone number: 33 442 90 85 12 – Fax number: 33 442 90 85 15

E-mail address: olivier.boutin@univ-cezanne.fr

ABSTRACT

Wet air oxidation process is used to treat wastewater with high chemical oxygen demand. Temperatures up to 350°C and pressures up to 30 MPa, are operated to develop a non-catalytic process. In the literature, there is some data about the phase equilibrium of water-air system but on larger domains and not accurate enough in our range. To study the process, it is necessary to complete the data with adapted pressures, temperatures and compositions. An experimental set-up has been developed to realize equilibrium measurements as well as trials on waste degradation. It consists of a stirred reactor of 150 mL equipped with two sapphire windows (diameter 4.1 cm) allowing a total visualization of the reactive chamber. A motorized pump assures the precision of the injections of components (liquid and gas). A hot/cold regulation system is also implemented. The results of experiments give the volume occupied by the liquid and the gas phases, for a combination of temperature, pressure and global composition. Measurements are realized to establish dew curves for water-air, water-nitrogen and water-waste-nitrogen systems. Nitrogen has the same behavior as Oxygen and can replace it in mixtures for the phases equilibrium studies with the waste to avoid any reaction. The presence of the waste, in the concentrations studied, has no significant influence on the equilibrium points. Those data serve to model the liquid-vapor equilibrium in the appropriate domain first with an ideal model and then with equation of state Soave-Redlich-Kwong and appropriate mixing rules. Those equilibrium models are then included in commercial engineering software to simulate WAO processes. With the objective to develop a process energetically optimized, the second part of this work is dedicated to perform exergy balances for each component and for the whole process.

INTRODUCTION

In a world context of legislations intensification on the environmental protection, it is necessary to improve the processes of urban water treatment and industrial aqueous effluents. Domestic waste water comes from various domestic uses of water. They are essentially carriers of organic pollution (cleaners, fats, solvents, organic molecules). Industrial waters have characteristics which vary from an industry to the other one (refineries, distilleries, pharmacy, microelectronics …). Besides organic, nitrogenous or phosphorous matters, they can also contain toxic products, solvents, heavy metals, organic micropollutants and hydrocarbons. The Wet Air Oxidation (WAO) can be adapted to these problems of treatment. It consists in oxidising the organic fraction of an effluent containing a strong concentration of

organic matter not biodegradable (Chemical Oxygen Demand COD lasts from 10 to 150 g.L^{-1}). For this process, an oxidizer (air, pure oxygen, peroxide of hydrogen) is put in contact with the liquid effluent. WAO processes work in sub-critical conditions: pressure between 1 and 20 MPa and temperature between 100 and 320°C. The strong pressures allow maintaining the oxidation reactions in the liquid phase.

The first stage of this process is thus the transfer of gaseous oxygen towards the liquid phase. During the conception of a WAO process, it is necessary to consider if oxygen quickly spreads towards the liquid phase. A basic work to develop this process is the thermodynamic equilibrium that can be reached between the constituents of the phase gas and the liquid phase. In particular the knowledge of phase equilibria water - air is necessary. In order to recover a maximum of energy, the choice of the industrial equipments will depend in particular on respective quantities of gas and on liquid going out of the reactor. The knowledge of the balances of phase water - air at first, but also in the presence of a 3rd compound representing the waste (acetic acid, phenol, etc.), will allow to choose the most adapted conditions of pressure and temperature. In this last case, in order to have no chemical reactions during the measurement, it is necessary to work with water / nitrogen system and to validate that they have an identical behaviour with water / air system.

For the existing experimental data, we can mention Heidemann [1] who measured the quantity of water in nitrogen and in the mixtures CO2 / N2, according to the temperature and the pressure. Before that, Himmelblau [2] studied the solubility of inert gases in water. Closer to our works, studies carried out by Japas and Franck [3] [4] concern the systems water - oxygen and water-nitrogen. Their experimental data are often used to estimate various parameters of equations of state. They were made by trials conducted in a cylindrical autoclave (volume: 95 mL) equipped with two sapphire windows, between 150 and 300 °C, and 20 to 270 MPa. These studies showed a similarity in the behaviour of two mixtures nitrogen / water and oxygen / nitrogen. However, their range of pressure being higher than that of WAO (until 35 MPa), their curves are thus difficult to exploitable in our operating domain. In is necessary to develop an accurate method in our experimental domain.

MATERIALS AND METHODS

Materials

The experimental design used is presented on Figure 1. It consists mainly of a view cell with a volume of 150 mL. This system can reach a maximum pressure of 300 MPa and maximum temperature of 350 °C. The system is regulated for the pressure with a high pressure syringe pump and for temperature with a cooling jacket and an electric heater. A stirring system allows a very good mixing of the medium. Sapphire windows allow visualising the entire volume of the cell, recorded with a CCD camera. The camera is used to detect the transition between a biphasic state gas/liquid with a monophasic liquid state.
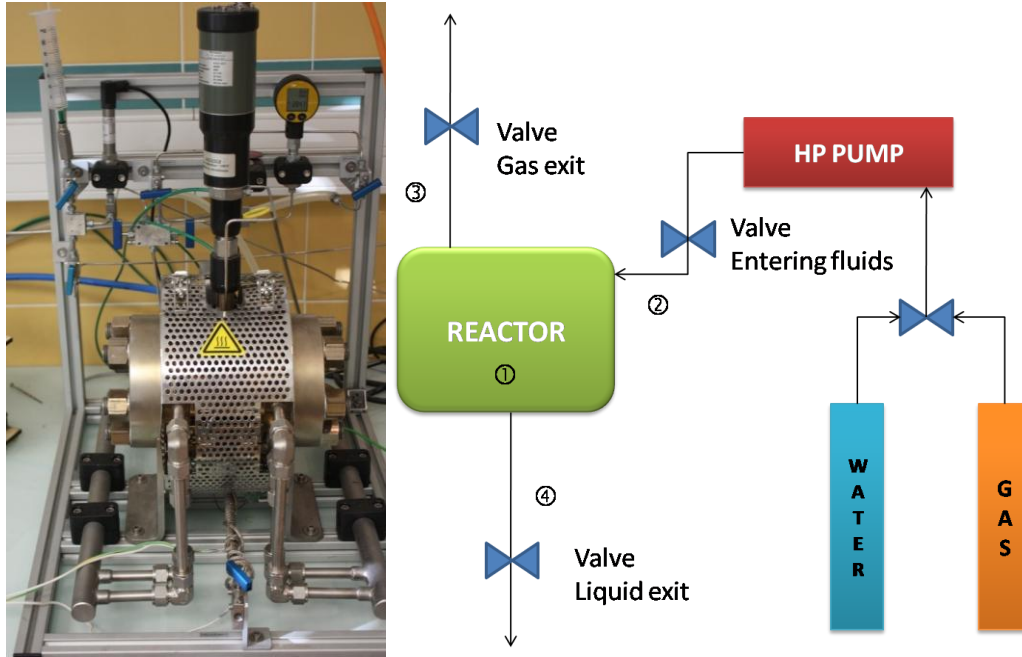
Figure 1 Experimental set-up for the measurement of phase equilibria

Experimental procedure

The experimental procedure is the following. In the case of the study of a water - nitrogen system for example, it is necessary to fix at first the quantity of initial water to be introduced and the molar water fraction in the mixture. The initial nitrogen pressure is then calculated to reach the desired zone of temperature and pressure. The nitrogen introduced by the pump is at 20°C. By using a table of the molar volumes molar of nitrogen at 20°C according to the pressure (calculation made by the equation of state of Soave-Redlich-Kwong and compared with the NIST database), we obtain the initial pressure of nitrogen in the cell. The cell is first pressurized to approximately 2 MPa, to stick windows sapphire and avoid any problem of leaks during the heating of the system. All the circuit around the pump (arrival pipes water tank, 50 cm^3 pump cylinder and pipe towards the optical cell) is then filled with water and pressurized, and the quantity of chosen water is injected in the cell. Once the cell isolated (zone 1 - 4 on Figure 1), the pump circuit is purged with nitrogen, then nitrogen pressure in the cell is increased until it reach the calculated pressure.

Thermodynamic calculations

As mentioned by Ji [5], attention has been paid to the modelling of the Henry constant and thanks to the equation of state reliable fitting was provided. Nevertheless testing those equations for dew point gives important gaps with data. In this work two models have been used in order to represent the experimental data obtained.

From a general point of view, dew point can be calculated by considering the general equilibrium between phases. For a gas - liquid equilibrium the simple relation to solve is the fugacity equality:

$$f_i^x = f_i^l \tag{1}$$

Ideal model

The so-called ideal model is based on the Raoult law stipulating that "the partial pressure in the gas phase is proportional to the molar fraction in the liquid phase". Activity coefficients being chosen equal to unity, a general definition is given by the following equation:

$$P = \sum_i P_i^\sigma x_i \tag{2}$$

The equation of state for the gas phase is again the ideal gas law. Below the water critical point, for a given temperature, the dew point being well defined, the calculation can be directly realised. The nitrogen being supercritical in the studied domain, it acts more as a "permanent" gas.

Model using Equation of State

Using equation of states consist by defining from the equation of state of the pure component an equation of state for the mixture and then by solving this equation of state to calculate the fugacity coefficients for both components and both phases. The equilibrium definition is then given by:

$$\varphi_i^l x_i = \varphi_i^g y_i \tag{3}$$

The equation of state used is the Soave Redlich Kwong one.

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V+b)} \tag{4}$$

The mixing rule is the MHV2 coupled with the UNIFAC group interaction parameters. It consists in calculating the parameter $a\alpha$ of the equation of state by deriving them from an activity model coefficient. This mixing rule is strongly recommended for calculation close to critical point and for mixture including polar and non polar molecules. The complete mixing rules description can be found in Michelsen [6].

EXPERIMETAL RESULTS AND MODELLING

The experimental results obtained with the view cell are presented on Table 1. In this Table are presented the different operating conditions: initial volume of water placed in the view cell, the initial nitrogen pressure, the resulting water molar content. The experimental result indicates the pressure and the temperature corresponding to the transition between a biphasic and a monophasic state.
The conditions tested in particular for pressures between 12 and 30 MPa, which are the most employed conditions for Wet Air Oxidations processes.

The thermodynamic modelling results are shown on Figure 2 for a water molar fraction of 0.62 and on Figure 3 for water molar fractions of 0.8 and 0.85.

Operating conditions			Transition conditions	
Water (mL)	Inital nitrogen pressure (MPa)	Water molar fraction	P (MPa)	T (°C)
9	1.51	0.85	12.61	325
11	1.88	0.85	15.27	341.9
12	2.11	0.85	15.95	343.7
9	2.11	0.8	16.62	348
8	1.88	0.8	14.08	330.7
7	1.67	0.8	11.63	317.3
10	2.4	0.8	17.75	351.3
11	6.61	0.62	28	348
10	6	0.62	26.15	345.8
9	5.4	0.62	22.74	336.8
8	4.8	0.62	20.55	335.9
8	4.8	0.62	19.67	336.9
9	5.4	0.62	22.38	337.8

Table 1 Experimental results

Even if the ideal model seems simple and out of scope, in the studied domain of the WAO process, the results given by the ideal model are the closest that can be obtained for the dew PTx data. Comparison of both models can be seen on Figure 2 and Figure 3. The ideal model is always closer to experimental data. For a given pressure, temperature gaps reach 10 °C for the ideal model but can increase to 30°C for the EOS model. Errors due to molar fraction estimation can be view on Figure 2 where results with a ± 0.02 absolute error are presented and on Figure 3 with a ±0.05 absolute error. The difference is not so high to explain the difference due to the model and for a same model, the difference with experimental data.

When water molar fraction increases to unity both models tend to superpose (see curve for x=0.9 on Figure 3), and of course to join the saturated properties of water.
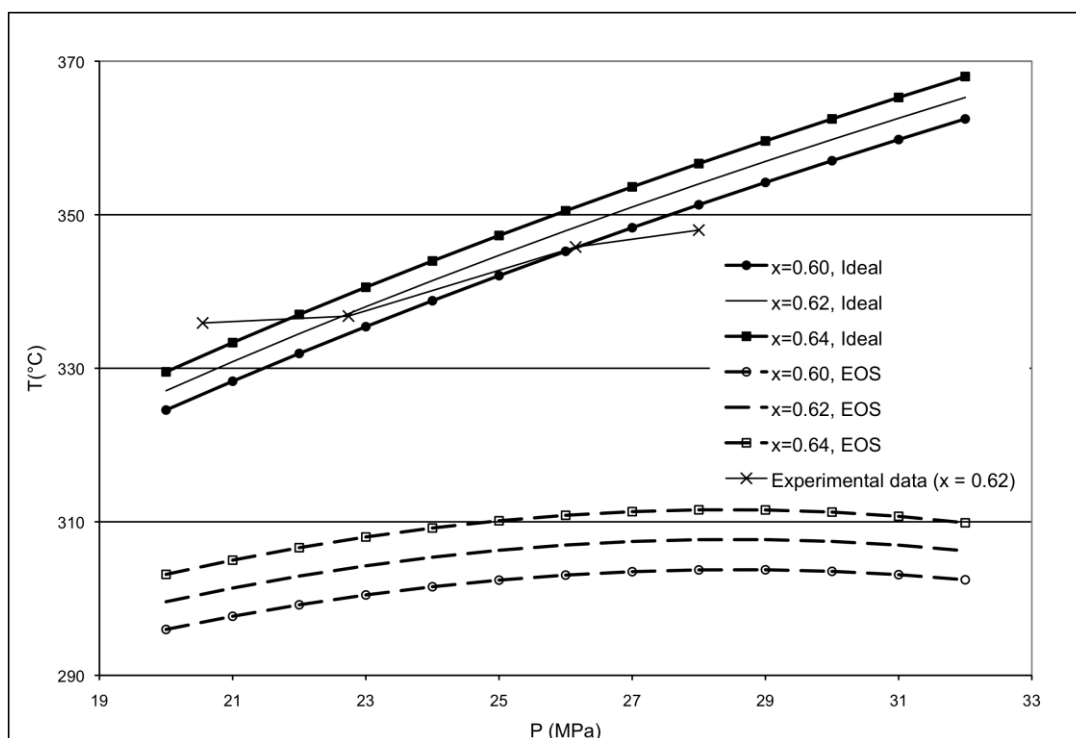

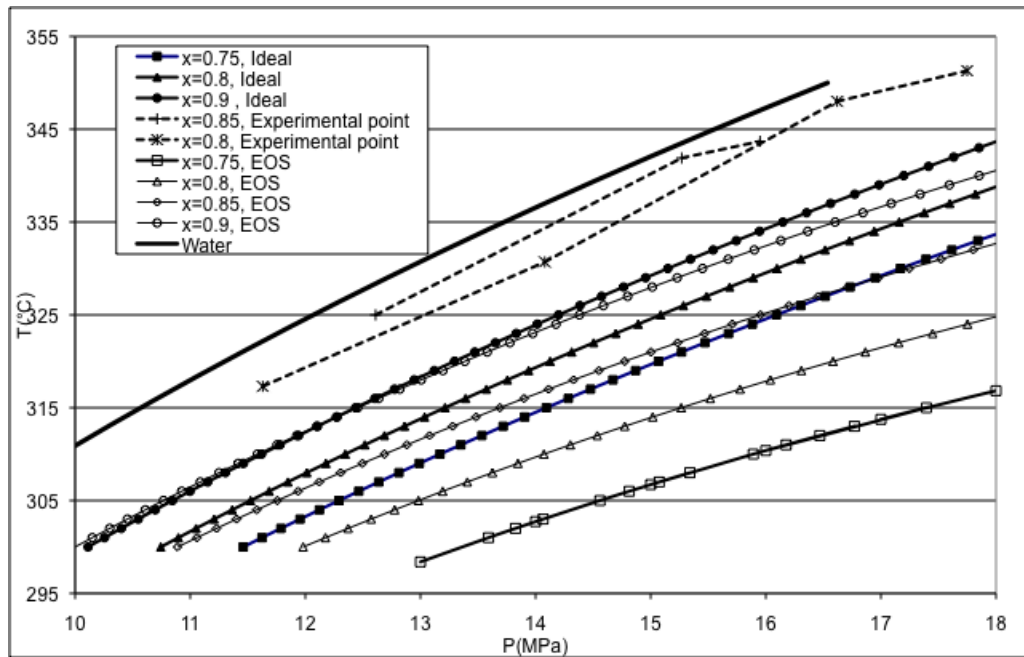**Figure 2: Comparison of models and experimental points for x_{water} = 0.62 including molar fraction error**

Figure 3: Comparison of models for x_{water} = 0.8 and 0.85 including molar fraction error and pure water saturation curve.

CONCLUSION

WAO processes are operated by pressure and temperature. One of the leading points for the success of oxidation is to avoid that the fluid phase disappeared. Oxidation leading to gas formation, the fraction of gas increases during reaction, meaning that for a given temperature, pressure would have to be increased. In order to manage the process functioning, it is important to implement a thermodynamic model in a process simulator. Taking into account our experimental obtained in the range of the process operation, different thermodynamic models have been tested. The conditions of pressure and temperature being not very far from the critical point of water, it is difficult to obtain an accurate modelling. Finally, the best result has been obtained with an ideal model.

REFERENCES

[1] HEIDEMANN, R.A., PRAUSNITZ, J.M., Industrial and Engineering Chemistry, Process Design and Development, Vol. 16, **1977**, p. 375.
[2] HIMMELBLAU, D.M., J. Chem. Eng. Data, Vol. 5, **1960**, p. 10.
[3] JAPAS, M.L., FRANCK, E.U., Ber. Bunsenges. Phys. Chem., Vol. 89, **1985**, p. 1268.
[4] JAPAS, M.L., FRANCK, E.U., Ber. Bunsenges. Phys. Chem., Vol. 89, **1985**, p. 793.
[5] JI, X., LU, X., YAN, J., Fluid Phase Equilibria, Vol. 9, **1990**, p. 21.
[6] MICHELSEN, M.L., Fluid Phase Equilibria, Vol. 222, **2004**, p. 39.