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Energy Optimisation of Wet Air Oxidation Process Based on the Preliminary Study on Liquid-Vapour Equilibrium

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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 realise 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. 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 realised to establish dew curves for water-air, water-nitrogen and water-waste-nitrogen systems. Nitrogen has the same behaviour 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-vapour 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 optimised, the second part of this work is dedicated to perform energy balances for each component and for the whole process.

1. 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). The Wet Air Oxidation (WAO) can be used for 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 oxidiser (air, pure oxygen, peroxide of hydrogen) is put in contact

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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 point important to be considered for the process scaling is the transfer of gaseous oxygen towards the liquid phase. A basic important study is hence the thermodynamic equilibrium behaviour between the gas and the liquid phases. 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. It is also important to consider the presence of a 3rd compound representing the waste (acetic acid, phenol, etc.), in order 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 et al. (1977) who measured the quantity of water in nitrogen and in the mixtures CO2 / N2, according to the temperature and the pressure. Before that, Himmelblau (1960) studied the solubility of inert gases in water. Closer to our works, studies carried out by Japas and Franck (1985a, 1985b) 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.

2. Materials and methods

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 **c**ooling 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.

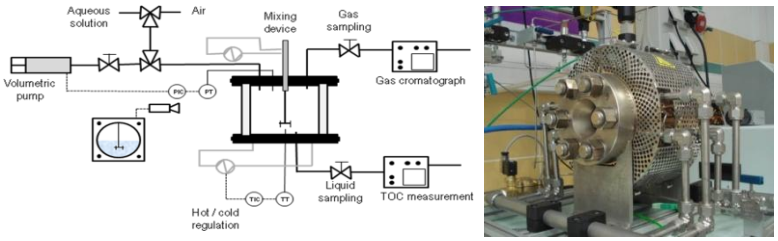

Figure 1: Experimental set-up for the measurement of phase equilibria

The experimental procedure is the following. In the case of the study of a water - nitrogen system, it is first necessary to fix 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 necessary initial pressure of nitrogen in the cell. The cell is first pressurised 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, the pump circuit is purged with nitrogen, then nitrogen pressure in the cell is increased until it reach the calculated pressure.

As mentioned by Ji et al. (2004), 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. The equation of state used is the Soave Redlich Kwong one.

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V+b)} \quad (1)$$

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 (1990).

3. Experimental results and modelling

Different operating conditions have been used: initial volume of water placed in the view cell, initial nitrogen pressure, 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.

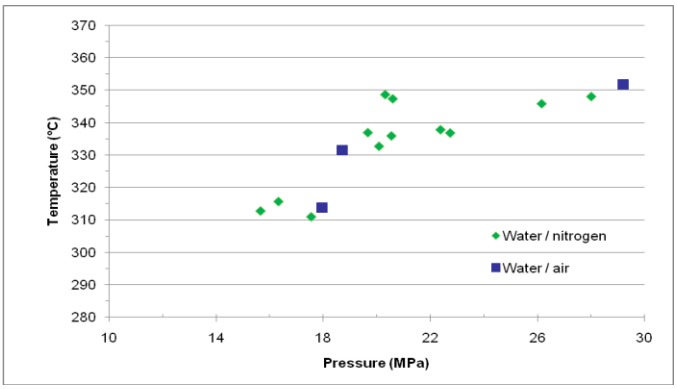

Figure 2: Experimental phase equilibriums and modelling simulation for water - nitrogen and water - air binaries for different water composition.

Different water molar fractions have been tested. Figure 2 presents the results obtained for two binary systems: water with nitrogen and water with air. It could be seen that the behaviour are nearly the same. That means that it is possible to use nitrogen alone for the determination of the equilibrium with the presence of a waste, in order to avoid its reaction. The results obtained for the ternary system water - nitrogen - waste (phenol or acetic acid, which is a degradation molecule) are presented on Figure 3. It could be seen that the presence of the tested wastes do not influence the phase equilibria, which is interesting when reaction occurs.

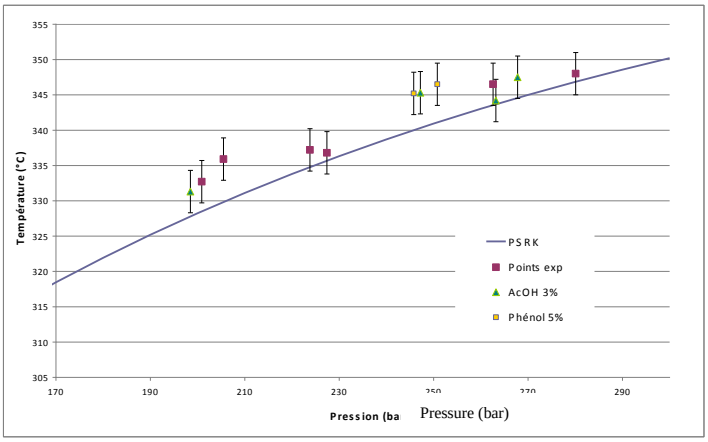

Figure 3: Experimental phase equilbria for water - nitrogen - waste ternary systems for different water composition.

4. Experimental design method

Experimental design is a statistical method that consists in selecting and ordering experiments to identify the quantitative effects of the chosen parameters on the responses of the system. The objective of the study is to explore the relationships between the chosen parameters of the process and the three responses (the energetic values) by using a sequence of experiments in order to obtain an optimal response. This kind of design will be called "numerical design". The production of the experiment plan and the interpretation of results has been done with, the NEMRODW software (2000-D, LPRAI Corporation, France). The four parameters are: temperature, pressure, air ratio and COD. To estimate the coefficients of the model, a Box Benhken design was chosen. The variation domains are the following: pressure (20-30 MPa); temperature (200-300 °C); COD (23-143 $g.L^{-1}$); air ratio (1.2-2); temperature of steam (160-200 °C). The experiment plan contains 42 simulations.

We have calculated three energetic values: exergetic efficiency, work balance and minimum heat required (or furnished) by the process evaluated by Pinch analysis for different process configuration. The exergetic efficiency η is the ratio between exiting exergies (turbines, streams, heat exchanges) and entering exergies (compressor, volumetric pump, heat exchanges, streams). The work balance ΔW is a non conventional parameter. It is the sum of power used to pressurize (compressor, pump)

and power recovered (turbines). If this term is negative, some work could be really recovered. Finally the third energetic value is the minimum hot utility requirement (Q_{Hmin}) which is evaluated using Pinch analysis. It corresponds to the energy which must be supplied by utilities (electric heating, hot oil or gas circuit, etc.). The Pinch analysis allows optimising the use of energy for various processes, in different fields of industry: chemistry, petrochemistry, refining and food-processing industry.

The estimation of the model coefficients is done using multi-linear regression. For the three responses, all the results are taken into account after analysing the statistical tests of significance for the model and for the different coefficients of the linear regression.

For the exergetic efficiency the regression is significant. The linear model (polynomial of 2^{nd} order) is hence validated. The same conclusions can be derived from the results obtained for Q_{Hmin} and work balance.

η decreases until a minimum, corresponding to a medium value of COD. The other parameters have no significant influence. Concerning Q_{Hmin}, two parameters have an influence: temperature and pressure. With this kind of conditions, the liquid phase is favoured at the reactor exit. A less important part of the reaction exothermic energy is lost to vaporise water in the reactor and heat is produced by the process. Finally, the work balance is mainly influenced by COD and temperature. The best negative values (work recovery) are obtained for the highest values of temperature and medium COD.

The experimental design allows the calculation of the desirability for the 3 energetic values in order to reach an optimum (Figure 4). This function is a multicriteria mathematical optimisation based on the different polynomial obtained from the numerical design. It necessitates giving the desirable values for each energetic parameter and a range of forbidden values. The optimisation will determine the maximum response values in the determined ranges. For each response, a chosen range is specified with forbidden values (exergetic yield < 0.6, Q_{Hmin} > 0 W, WR > 0 W) and target values (exergetic yield = 1, Q_{Hmin} = -50 W, WR = -15 W).

From an energetic point of view of the process, this optimum is considered as the good conditions of functioning.

In this study, the values obtained are a pressure of 20.5 MPa, a temperature of 294 °C, an aeration ratio of 1.7 and a chemical oxygen demand of 47.6 $g.L^{-1}$. In these conditions, the exergetic efficiency is 0.7, QH_{min} is -8.1W and work balance is -12,1W. This method of energetic optimization based on coupling process simulation and experimental design is validated. By improving process flowsheet with technologies of energy recovery, updating the technical data according current industrial equipments, and achieving kinetic studies on phenol degradation to take in account the conversion rate of the waste, this method will be relevant for the development of a non-catalysed WAO process energetically optimised, but for other kind of industrial processes as well.

5. 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. Besides, the method of energetic optimization based on coupling process simulation and experimental design is validated and proved to be a fast, efficient and interesting tool for process evaluation. By improving process flowsheet with technologies of energy recovery, updating the technical data according current industrial equipments, and achieving kinetic studies on phenol degradation to take in account the conversion rate of the waste, this method will be relevant for the development of a non-catalysed WAO process energetically optimised, but for other kind of industrial processes as well.

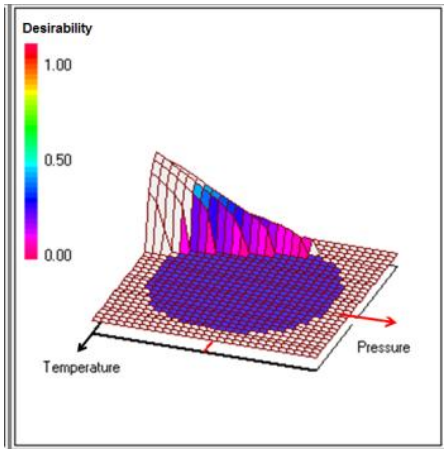

Figure 4: Evolution of the desirability function with temperature and pressure variation.

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