DESIGN OF AN AUTOMATED FIXED BED REACTOR USED FOR A CATALYTIC WET OXIDATION PROCESS

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Abstract: Treatment of polluted industrial wastes is one of the challenging research topics that occupy an important position in various chemical processes. Wet Air Oxidation (WAO) is one of the emerging processes suited for the treatment of special aqueous wastes. The system consists of an oxidation in the liquid phase of the organic matter by molecular oxygen at high temperature (200-325°C) and high pressure (up to 175 bar). It is an enclosed process with a limited interaction with the environment as opposed to incineration. In this paper, we will discuss the setup and the design of an automated fixed bed reactor used for wet oxidation of various types of wastes. The system is controlled by a set of intelligent sensor modules used for data acquisition. Regulation loops integrated within the sensor modules had been developed in order to control the gas flow, the reactor temperature and the liquid sampling part. The process supervision and monitoring had been achieved through the deployment of a SCADA software application. The graphical interface developed for this purpose monitors the major parts of the process.

1 INTRODUCTION

The identification of highly refractory and non-biodegradable organic pollutants in wastewater, especially coming from the chemical and petrochemical industry, has challenged the conventional wastewater treatment such as incineration or biological abatement. There is a clear need to test and set-up an emerging alternative technology that can deal with highly concentrated and/or toxic non-biodegradable organic water pollutants. However, it seems impossible in the close future to dispose of one universal method able to destroy all of the detected pollutants at an acceptable cost (Masende, 2003). Therefore, Wet Air Oxidation (WAO) is an efficient process by which organic pollutants can be transformed by oxidation under high pressures (50-250 bar) and high temperatures (200-325°C), into carbon dioxide and water (Mishra, 1995). The process can be performed under milder conditions (temperatures and pressures) by using a homogenous or heterogeneous catalyst. Catalytic Wet Air Oxidation (CWAO) is thus an attractive process for wastewater treatments of toxic pollutants such as phenol, pesticides, methyl *tert*-butyl ether (MTBE) and their intermediate oxidation compounds (Pintar, 1992).

Several studies with noble metal catalysts, mainly Ru and Pt supported on carbon, Al_2O_3, TiO_2 and CeO_2 have revealed their stability and capacity to destroy organic pollutants (Imamura, 1988). In contrast to platinum, ruthenium was found to be an active metal during the oxidation of acetic acid, which is very refractory. Comparison of Ru/CeO_2 and Ru/TiO_2 showed that titanium oxide was more stable in acetic and oxidizing medium, but the loading of Ce on the catalyst significantly changes the surface properties resulting in a better dispersion of the noble metals. Thus, Ruthenium and Cerium metals supported on alumina are considered to be stable, accurate and cost effective catalysts (Oliviero, 2000). There are only some tens of industrial plants in the world and very few documents are available for the scientific design of

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such processes due to their complexity and the delicacy needed for their proper operation (Debellefontaine, 1999). Therefore, in this work we will show the essential techniques and equipments allowing us to control and monitor a pilot scale reactor designed for the wet oxidation of organic pollutants.

After presenting the system architecture and the communication interface, we will attempt to emphasize on the use of intelligent sensor modules in order to adequately control the reactor temperature and pressure as well as the gas flow and the liquid outlet.

2 SYSTEM ARCHITECTURE AND COMMUNICATION

The installation (Figure 1) consist of an L-316 tubular fixed-bed reactor (7.6 cm internal diameter and 70 cm in length), which is placed in the center of an oven implementing an electrical resistor controlled by a PID controller. The solution is introduced to the reactor by a high-pressure pump at a flow rate ranging from 1 to 10 $cm^3.min^{-1}$. The catalyst is placed between two layers of glass beds in the reactor. The oxygen is directly fed from a high-pressure bottle whereas a gas flow indicator and controller (FIC – Brooks) controls its flow rate. The effluent of the reactor passes through two condensers and a gas-liquid separator. The gas phase is released in the hood after passing through a gas flow indicator (FI – Brooks) and the liquid phase is stored in a tank whereas a level indicator (LI – Bamo) controls a regulation valve (LV - Samson) prior to liquid evacuation. A backup pressure regulator (PIC) placed at the gas outlet maintains a stable pressure inside the system.

Sensors and actuators are plugged into a set of four intelligent sensor modules (ISM112 – Gantner) interconnected through an RS485 field bus. An RS232/RS485 converter enables the supervision station to communicate with the sensor modules using the Modbus RTU protocol. The intelligent sensor module supports measuring methods with 2-, 3-, and 4-wire technique and measuring methods with 4- and 6-wire bridge connection. Consequently, the most varying measurement tasks can easily be solved by means of the different analog inputs and in combination with the force output, which provides the local power supply for the transducers. The module can simultaneously take up and process sensor signals from several heterogeneous sensors. As many sensors can be connected as there are analog and digital signal inputs and outputs available. With the ISM112 these are 6 sensors at the most, 4 analog and 2 digital sensors. The RS485 interface permits the simultaneous connection and operation of a maximum of 32 bus users per segment. Among analog and digital signal processing; the intelligent sensor module can handle a controller variable by which a sensor variable can be monitored for a definable set value. Deviations of the sensor variable’s value will be corrected depending on the set function of the controller (PID-controller) and will then be assigned to the controller variable. This corrected value can be assigned to an analog output and then be used to influence the input signal by a corresponding connection. Accordingly, we were able to control and monitor most of the system parameters in order to boost and optimize the reaction conditions. A set of five thermocouples indicates the temperatures at different levels of the process, especially at the center of the reactor where the temperature had been adequately controlled and monitored. Pressure indicators monitor the system global pressure required for the reactor proper operation. Possible fluid leakage can be detected through pressure drops inside the system. Gas flow is controlled by an algorithm set by the manufacturer whereas the intelligent sensor modules directly control the reactor temperature and the regulation valve through a set of regulation parameters defined by the *Ziegler-Nichols* method.

3 TUNING A PID CONTROLLER

The first step in the design strategy is to install and tune a PID controller (Tan, 2006). The ideal continuous PID controller returns the controller output u, as given by equation (1), where K_p is the proportional gain, T_i is the integral time, T_d the derivative time, and e the error between the reference (*ref.*) and the process output (y).

$$u = K_p \left(e + \frac{1}{T_i} \int_0^t e.dt + T_d \frac{de}{dt} \right) \tag{1}$$

We are concerned with small sampling periods T_s, the equation may be approximated by a discrete approximation. Replacing the derivative term by a backward difference and the integral by a sum using rectangular integration, an approximation may be given by the equation (2).

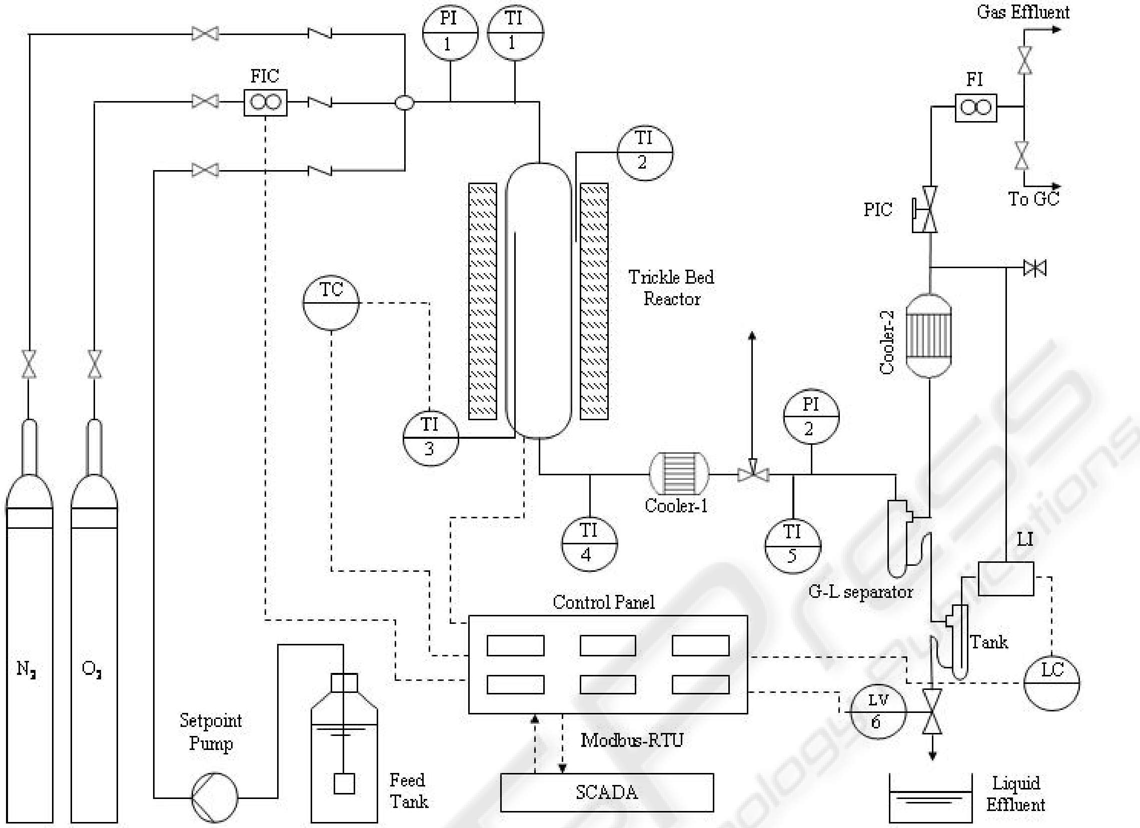

Figure 1: Wet Air Oxidation process diagram. Abbreviations: FI: Flow indicator; FIC: Flow indicator and controller; GC: Gas Chromatography; LC: Level controller; LI: Level indicator; LV: Regulation valve; PI: Pressure indicator; PIC: Backup pressure regulator; SCADA: System control and data acquisition; TI: Temperature indicator.

$$u_n = K_p\left(e_n + \frac{1}{T_i}\sum_{j=1}^{n} e_j T_s + T_d\,\frac{e_n - e_{n-1}}{T_s}\right) \qquad (2)$$

Index n refers to time instant. By tuning we shall mean the activity of adjusting the parameters K_p, T_i and T_d. Several tuning aspects may be illustrated by static considerations. For purely proportional control ($T_d = 0$ and $1/T_i = 0$), the control law (2) reduces to the following equation:

$$u_n = K_p.e_n \qquad (3)$$

Considering the feedback loop in Figure 2, where the controller has the proportional gain K_p and the process has the gain K in steady state, the output x can be related to the reference (*ref.*), the load l, and the measurement noise n by the following equation:

$$x = \frac{K_p K}{1+K_p K}\left(ref - n\right) + \frac{K}{1+K_p K}\,l \qquad (4)$$

If n and l are zero, then K_p should be high in order to insure that the process output x is close to the *ref.* Furthermore, if l is nonzero, a high value will make the system less sensitive to changes in the load l. But if n is nonzero, K_p should be moderate otherwise the system will be too sensitive to noise. Obviously, the setting of K_p is a balance between: stability, noise sensitivity, and load regulation.

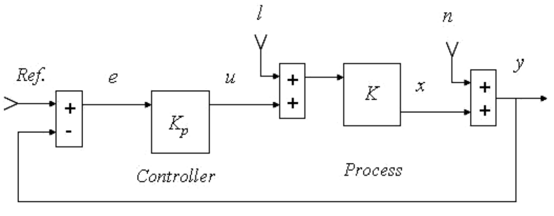

Figure 2: Closed loop system identification.

A PID controller may be tuned using the *Ziegler-Nichols frequency response method*, according to the following procedure:

(a) Increase the proportional gain until the system oscillates (Figure 3); that gain is the ultimate gain K_u.

(b) Read the time between peaks T_u at this setting.

(c) Approximate values for the controller parameters are given in a table.

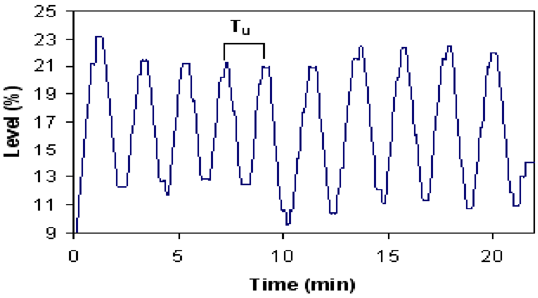

Figure 3: Ziegler-Nichols frequency response method.

The sample period may be related to the derivative gain T_d. In connection with the *Ziegler-Nichols* rules, this implies that T_s should approximately be equal to 1 – 5 percent of the ultimate period T_u. Taking full advantage of this method; we were able to adequately control the reactor temperature and the liquid evacuation unit. When the system reaches the steady state, the controller allows us to maintain a constant liquid level in the tank. Consequently, liquid flow can be continuously evacuated at the system's outlet.

4 HUMAN MACHINE INTERFACE (HMI)

An operator's graphical interface was developed using the FIX MMI Intellution SCADA software which combines high performance monitoring and control with wide range of data acquisition on the Windows NT/2000/9x operating systems. The FIX application contains three sets of multithreaded processes: the user process (HMI), the FIX engine and the industrial automation device servers. These processes interact through a client-server relationship. The user process displays the user interface and executes blocks of code that are defined for control algorithms, supervisory control, analysis and visual presentation. The event-driven engine maintains a real time database, communicates with device servers and performs a multitude of tasks including engineering unit scaling, alarm processing and historical data collection and trending. Device servers are the applications that communicate with Input/Output devices. The FIX application establishes a communication with the ISM112 intelligent sensor modules through the deployment of a Modbus RTU server fully compliant with the latest Modbus RTU protocol definitions. Therefore, the ISM112 data registers can be accessed and modified to the desired values allowing thus the operator to have full control of the process variables.

5 CONCLUSION

The aim of this work is to setup an oxidation process that meets the conditions needed for the aqueous destruction by oxygen or air of organic pollutants. The aforementioned techniques and equipments which in priority are based on regulation and automation procedures, allowed us to design an automated fixed bed reactor that fulfills the required temperatures and pressures conditions (up to 300°C and 25 bar) usually used for CWAO processes. The developed monitoring interface allows the operator to easily manage and control the process parameters. Chemical runs allowing us to validate the system efficacy during the oxidation of various types of aqueous wastes, are in process of completion.

REFERENCES

Debellefontaine, H., Foussard, J.N.,Wet air oxidation for the treatment of industrial wastes, *Waste Manage.*, 20 (2000) 15.

Imamura, S., Fukuda, I., Ishida, S., Wet oxidation catalyzed by ruthenium supported on cerium(IV) oxide, *Ind. Eng. Chem. Res.*, 27 (1988) 718.

Masende, Z.P.G., Kuster, B.F.M., Ptasinski, K.J., Janssen, F.J.J.G., Katima, J.H.Y., and Scouten, J.C., Platinium catalysed wet oxidation of phenol in a stirred slurry reactor: A practical operation window, *Appl. Catal. B*, 41 (2003) 247.

Mishra, V.S., Mahajani,V.V., Joshi, B., Wet Air Oxidation, *Ind. Eng. Chem. Res.*, 34 (1995) 2.

Oliviero, L., Barbier Jr, J., Duprez, D., Guerrero-Ruiz, A., Bachiller-Baeza, B., Rodriguez-Ramoz, I., Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru–CeO_2/C catalysts, *Appl. Catal. B*, 25 (2000) 267.

Pintar, A., Levec, J., Catalytic oxidation of organics in aqueous solutions : I. Kinetics of phenol oxidation, *J. Catal.*, 135 (1992) 345.

Tan, W., Liu, J., Chen, T., and Marquez, H.J., Comparaison of some well-known PID formulas, *Comput. Chem. Eng.*, 30 (2006) 1416.