UNIVERSITAT POLITÈCNICA DE CATALUNYA

ESTUDIO DEL COMPORTAMIENTO DE REACTORES DISCONTINUOS Y SEMICONTINUOS: MODELIZACIÓN Y COMPROBACIÓN EXPERIMENTAL

Autor: M. Dolors Grau Vilalta
Director: Lluis Puigjaner Corbella

Septiembre de 1999

Anexo

En este apartado se presentan los resúmenes de las publicaciones más relevantes a que ha dado lugar esta Tesis, ordenadas cronologicamente y clasificadas en Revistas y Congresos.

Revistas

Grau, M.D. y L. Puigjaner. Batch and Semibatch Reactors Modeling and Validation Based on On-Line pH Measurement. *Chemical Engineering Communications.* In press (1999).

In this work a comparative study between batch and semibatch reactors performance has been carried out based on on-line pH measurement. The system chosen was an acid-base reaction, and the concentration of the species in the reactor was obtained by measuring the pH. The experiments were carried out in a glass-jacketed reactor of 5 l, provided with different sensors and a data acquisition system. Thermal studies were carried out previously by heating and cooling water, and also the kinetic equation of the reaction was established. Measures of the reaction mass pH, concentration profiles of reagents and products have been obtained and compared with those determined by simulation. An algorithm describing the mathematical model has been developed and implemented in a software module written in FORTRAN 77 language. This model has been validated with experimental results and will be further extended to contemplate complex control situations.

Grau, M.D.; J.M. Nougués y L. Puigjaner. Batch and Semibatch Reactor Performance for an Exothermic Reaction. *Chemical Engineering and Processing.* In press (1999).

In this work a study of a batch and semibatch reactor has been carried out based on a very exothermic reaction between thiosulfate and hydrogen peroxide. The experiments were carried out in a glass-jacketed reactor of 5 l, provided with different sensors and a data acquisition system. Thermal and kinetic studies were carried out previously using an adiabatic batch reactor. Then, these results have been used for experiments in semibatch mode of operation with heat transfer. Several experiments have been carried out at different operating conditions (addition flow, initial temperature, initial concentration of reagents...). In batch and adiabatic mode of operation, experimental measures of the reaction mass temperature provided concentration profiles of reagents and products which have been compared to those determined by simulation. In semibatch mode of operation, temperature profiles have also been simulated and validated with experimental results. An algorithm describing the mathematical model has been developed and implemented in a software module written in FORTRAN 77 language. With this mathematical model it has been possible to obtain concentration and heat profiles for the semibatch mode of operation.

Congresos

Grau, M.D.; A. Bonsfills; J.M. Nougués y L. Puigjaner. Kinetic and Thermal Studies in an Experimental Batch Reactor. ***Proceedings 7th Mediterranean Congress of Chemical Engineering*****. pp. 155, Barcelona (1996).**

Batch processes play a very important role in chemical process industry, having their main applications in the production of specialty chemicals, polymers or bioproducts. These processes are characterized not only by small scale flexible production and high added value products, but also by reaction systems that may be quite complex and not entirely known. For this reason batch reactors are also very used in studies of reaction kinetics and thermal effects modelling.

This work has been executed in a pilot plant consistent of a jacketed reactor provided with different sensors of temperature, pH and conductivity, which may take measures on-line. The temperature may be measured in the reactor mixture and in the fluid circulating through the jacket. A PC is employed for data acquisition and control of the experimental reactor.

The study consists of two parts. Initially, we have used the batch reactor to determine the kinetic equation of ethyl acetate saponification by measuring the conductivity variation of the solution at different temperatures, and we have obtained the Arrhenius equation. Finally, we have developed the mathematical models concerning thermal effects of this reactor which have been implemented in software supporting written in Fortran 77 language. The models have been validated with experimental results obtained by heating and cooling water through the jacket.

Grau, M.D.; A. Bonsfills; J.M. Nougués y L. Puigjaner. Comparative Study of Batch and Semibatch Reactors Performance. ***Proceedings 7th Mediterranean Congress of Chemical Engineering.*** **pp. 172, Barcelona (1996).**

High added value products (fine chemicals or pharmaceuticals) are typically manufactured in batch processes. Batch reactors are very used because of their flexible mode of operation and their similarity in principle to the laboratory glass reactor. Their dynamic nature is associated to variations in conditions during each cycle.

On the other hand semibatch reactors are also commonly used in the fine chemicals industry. In semibatch operation the volume of reaction mass varies, and it is more difficult to formulate reactor performance equations than in the case of batch reactors. But the semibatch reactor presents a lot of advantatges such as control of reaction, particulary important for highly exothermic reactions and safety questions.

This work compares the detailed mathematical models of the two operation modes carried out in the same reactor and considering the same reaction, with results obtained experimentally in a fully instrumented bench scale chemical reactor. The reaction studied is ethyl acetate saponification and the models are solved supported by software developed in Fortran 77. Finally, further studies are carried out in a more exothermic reaction using the semibatch reactor.

Grau, M.D. y L. Puigjaner. Simulation of Batch and Semibatch Reactor: Experimental Validation for an Exothermic Reaction. ***Proceedings 8th Mediterranean Congress of Chemical Engineering.*** **In press. Barcelona (1999).**

Batch reactors are very much used in studies of reaction kinetics and thermal effects modelling, but the course of the reaction can only be controlled by the heat-exchange system. Semibatch mode of operation can be used to have a best control of the reaction by the progressive addition of one of the reactants, and is particularly important for highly exothermic processes where safety is of high concern. In this work a study of a batch and semibatch reactor has been carried out based on a very exothermic reaction between sodium thiosulfate and hydrogen peroxide . The experiments were carried out in a glass-jacketed reactor of 5 l, provided with different sensors and a data acquisition system. Thermal and kinetic studies were carried out previously using an adiabatic batch reactor (1,2). Then, these results have been used for experiments in batch and semibatch modes of operation with heat transfer.

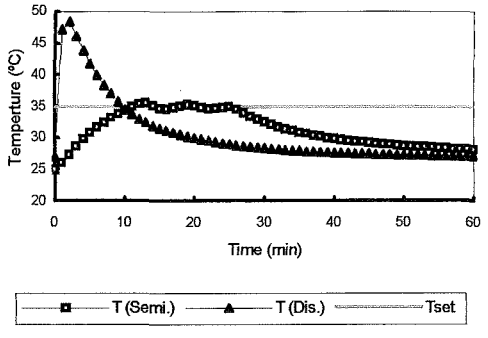

Fig. 1 Temperature profiles for batch and semibatch reactor.

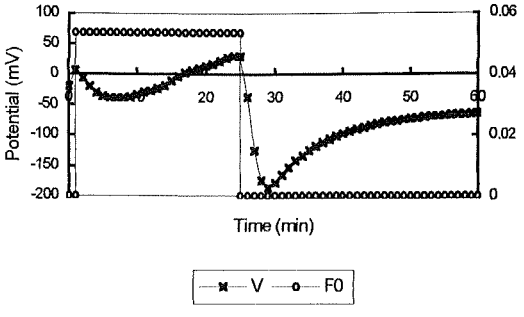

Fig. 2 Potential evolution and flow of H_2O_2 added in semibatch reactor.

An algorithm describing the mathematical model has been developed and implemented in a software module written in FORTRAN 77 language. When mathematical model has been validated with experimental results, it is possible to obtain by simulation, concentration and heat profiles for the semibatch mode of operation.

All experiments have been carried out in excess of $Na_2S_2O_3$. In the Figures 1 and 2 are represented experimental data obtained in the pilot plant. It is impossible, as it is shown in the Fig.1, to control the temperature reaction in the case of batch reactor. For the semibatch reactor (3) the set-point temperature is attached and maintained before the addition of H_2O_2 is finished (Fig. 2), but with reactants more concentrated it is also impossible to control the temperature.

The experimental results obtained in adiabatic operation have been very useful in work realised in semibatch mode of operation using the same reaction. Because the heat transfer is insufficient to remove heat generated by reaction, in further work it will be interesting to control the temperature of reaction by adding H_2O_2 with variable and controlled flow, in order to study safety aspects.

REFERENCES

(1) S.A. Vetjasa, R.A. Schmitz, An experimental study of steady state multiplicity and stability in an adiabatic stirred reactor, AIChe Journal, Vol. 16, No.3, 1970, p.410-419.

(2) K.F. Lin, L.L. Wu, Performance of an adiabatic controlled cycled stirred tank reactor, Chem. Eng. Science, Vol. 36, 1981, p. 435-444.

(3) F. Stoessel,Design thermally safe semibatch reactors, Chem. Eng. Progress, September 1995, p.46-53.

Grau, M.D.; J.M. Nougués y L. Puigjaner. Optimisation of the Inlet Flow in a Fed-Batch Reactor. *Proceedings 8th Mediterranean Congress of Chemical Engineering.* In press. Barcelona (1999).

The fed-batch reactor is commonly used in the fine chemicals industry. But since in semibatch operation there is no steady state, the volume of the reaction mass varies, causing a variation of the heat-exchange area. Thus, it is more difficult to formulate reaction performance equations than in the case of batch or continuous stirred-tank reactors (1). When a set-point is selected for the reaction mass temperature, it is possible to control the reaction by manipulating the feed rate of one of reactants, maintaining the inlet jacket temperature at a prefixed value.

In this work a very exothermic reaction has been chosen (2), feeding H_2O_2 (A) into $Na_2S_2O_3$ (B) solution, with a relationship $c_{B0} / c_{A0} = 2/3$. The experiments have been carried out in a glass-jacketed reactor of 5 l, provided with different sensors and a data acquisition system. First experiments have been realised to obtain temperature profiles of reaction mixture with different feed rates of H_2O_2 (Fig. 1). These experiments have been used to validate the mathematical model developed with MATLAB software. Necessary kinetic and thermodynamic data for the simulation have been determined in the same pilot plant in a previous work.

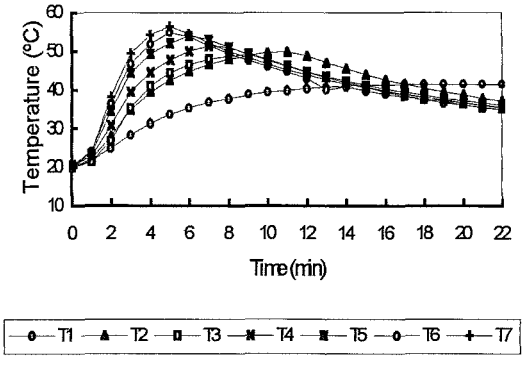

Fig. 1 Temperature profiles for different inlet flow.

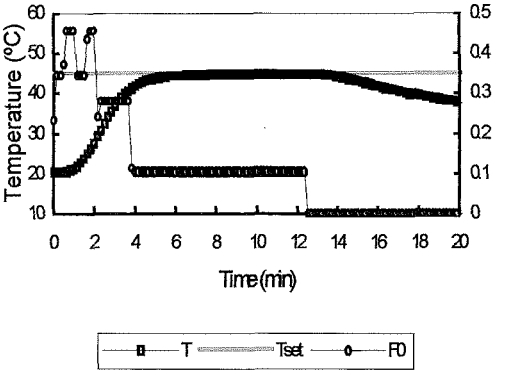

Fig. 2 Temperature and inlet flow optimised.

Then, an optimisation program has been developed to obtain the best combination of inlet flow and addition time, to maintain the reactor temperature under 45 °C (set-point temperature selected). The optimisation method chosen has been the Genetic Algorithms (3), based on the evolutionary process encountered in nature. This method is multivariable and begins with different points (*population*) in order to avoid falling in a local maximum. Within the genetic search, genomes are selected from the population. Genetic operators (*crossover* and *mutation*) are applied on the selected genome and the objective value is calculated. Some or all of the members of the new generation replace the current population depending on the value of the objective function (4). Figure 2 shows one case of the results obtained. Other combinations of addition time- inlet flow are possible with similar achievements.

REFERENCES

(1) P. Hugo, J. Steinbach , F. Stoessel, Calculation of the Maximum Temperature in Stirred Tank Reactors in Case of a Breakdown of Cooling, Chem. Eng. Sci., Vol. 43, No. 8, 1988, p. 2147-2152.
(2) F. Szeifert, T. Chovan, L.Nagy, Process Dynamics and Temperature Control of Fed-batch Reactors, Computers chem. Engng., Vol. 19, Suppl., 1995, p. S447-S452.
(3) J.H. Holland, Algortimos Genéticos, Investigación y Ciencia, septiembre, 1992, p. 38-45.
(4) T. Löhl, C. Schulz, S. Engell, Sequencing of Batch Operations for Highly Coupled Production Process: Genetic Algorithms Versus Mathematical Programing, Computers chem. Engng., Vol. 22, Suppl., 1998, p. S579-S585.

Nougués, J.M.; M.D. Grau y L. Puigjaner. Parameter Estimation with Genetic Algorithm in Control of Fed-Batch Reactors. *AIChE Annual Meeting.* In press. San Diego (1999).

Compared with continuous processes the control of batch processes is more difficult (operating conditions change with time, the same process unit are used for several different operations, etc.). However, the extraordinary flexibility of batch plants which allows fast adaptation to market demands together with the intensive development in hardware and computer process control, has prompted the fact that batch processes are gaining ground in chemical industries.

In this work, the temperature control strategy of a fed-batch reactor has been developed. The fed-batch operation can increase the productivity but may incur in reactant overdose, which in care of exothermic reaction would result in possible runaway condition.

These control problem are discussed by several authors and different solution approaches have been proposed. It is well known that the direct application of first principles models in the control algorithm is difficult and introduce additional problems due to the models complexity and the many a priori parameters involved; on the other hand the control algorithms based on the inverse of the plant model are verysensitive to model errors.

The control strategy presented follow the way of the tendency model concept (Filippi-Bossy et al.1989). The strategy considers two basic steps. In the first one, a simplified first principle model is adjusted with experimental data from previous batches using Genetic algorithm (GA). The model obtained is used to get the best feeding profile (temporal trajectory) to minimize the reaction time with a temperature constraint. The genetic algorithm has been also used for this task. In the second step, the optimized trajectory obtained in the previous step is used to drive the on-line control system.

A GA was used because it requires only information concerning the quality of the solution produced by each parameter set (objective function values). This differs from many optimization methods which require derivative information or, worse yet, complete knowledge of the problem structure and parameters. Since GA do not require such problem-specific information, they are more flexible than most search methods. The GA also differ from a number of search techniques in that they use random information to guide their search. Although random choices are used to define their decision rules, GA's are not random walks through the search space. They use random choice efficiently in their exploitation of prior knowledge to rapidly locate near-optimal solutions. Additionally, GA's consider many points in the search space simultaneously and therefore have a reduced chance of converging to local optima (C.L Karr E. J. Gentry,1993)

In GA's the natural parameter set of the problem must be coded as a finite string of characters. Also a fitness function must be defined to evaluate the sets of parameters (population). In this paper two optimization problems were solved with GA: 1) the model parameters identification and 2) the optimal feeding profile. The main task in GA application is the formulation of the string codings and its relation with parameters of the system, and the other important task is the evaluation function formulation (fitness function).

The system developed was validated by simulation and in a pilot scale reactor. The reaction used was the oxidation of Na2S2O3 with H2O2.. This is an exothermic oxidation reaction which has been studied by other authors in previous works. The pilot scale reactor is a 5 liter reactor, with a data acquisition system based on GPIB bus and PC software. As mentioned above the reactor was operated in fed-batch mode being the H2O2 feeded into Na2S2O3. All the software for on line control was developed in C and the system analysis and model parameters adjustment was made in Matlab developed modules.

References

Filippi-Bossy C. J Bordet, J. Vellermaux, S. Marchal-Brassely and C.
Georgakis Comp. Chem. Eng, 13,35-47, (1989).
Karr Charles L. and Edward J. Gentry, IEEE Trans. Fuzzy Systems, 1,1,46-53, (1993).