

SIMULATION AND OPTIMIZATION STUDIES OF CATALYZED ESTERIFICATION OF PROPIONIC ANHYDRIDE WITH 2-BUTANOL: BATCH VERSUS SEMI BATCH OPERATION

F.S. Rohman, S. Abdul Sata and N. Aziz*

School of Chemical Engineering
Universiti Sains Malaysia, Engineering Campus
14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

*Corresponding Author's E-mail: chnaziz@eng.usm.my

ABSTRACT

A model to represent the catalyzed esterification of propionic anhydride with 2-butanol has been developed and simulated. Two modes of operation i.e. batch and semi batch have been simulated and compared. The performance of both modes of operation has been compared using two performance indicators i.e. amount of conversion and process time. The effect of feed rate (semi batch) and temperature (both batch and semi batch) towards time required to achieve 97% of conversion has been carried out. Then the time required to achieve 97% conversion in semi batch operation has been optimized using Control Vector Parameterization (CVP) technique. It was observed that the highest conversion can be achieved at the lowest dynamic feed rate. For the effect of temperature, it was found that the process time of batch operation was shorter than in the semi batch if temperature is lower than 323 K, but at temperature greater than 333K, process time required by semi batch is shorter than the batch. For the optimization problem, the optimum temperature and feed rate trajectories obtained were led to shorter process time than batch operation i.e. 98 min for achieving 97% of conversion.

Keywords: Simulation; Dynamic Model; Batch and Semi Batch Catalyzed Esterification; Dynamic Optimization

1. INTRODUCTION

Sec-butyl propionate ester is a fragrance and flavors that widely used in food, cosmetic and pharmaceutical industries. The ester is commonly produced either in batch and semi batch reactors [Srinivasan *et al.*, 2003, Chang and Chen, 2004]. Usually, the ultimate goals of the process considered in batch and semi batch reactors are to improve the production quality, i.e. to maximize conversion; and to increase the process productivity, i.e. minimize the time required to achieve a required conversion. Since the dynamic nature of the batch or semi batch process may affect their quality, thus an understanding of the effects of simple physico-chemical factors on the kinetics of reaction systems is essential, especially the relationship of rate of reaction with concentration, temperature and feed rate (i.e., semi batch mode) during the reaction. At the same time, imposing an appropriate concentration and temperature profiles might improve the quality of the production. Meanwhile, for semi batch reactor, the feed rate may affect on both actual concentration rate and conversion [Vemuri, 2004, Sauvage, 2007].

Due to above reasons, the optimal parameter trajectory should be obtained in order to achieve the maximum productivity. A dynamic optimization technique is one of techniques available to determine trajectory because it can deal with the ordinary differential equations (ODE) which can represent a real behavior of dynamic process [Hirmajer, et al. 2010]. The numerical methods used to find a deterministic solution of dynamic optimization problems can be grouped into two categories: indirect and direct methods. In both categories, there are two strategies of direct method: sequential and simultaneous methods. In the simultaneous strategy, both the control and state variables are discretized using polynomials (e.g., Lagrange polynomials) of which the coefficients become the decision variables in a much larger Nonlinear Programming problem (NLP). In the sequential strategy, often called control vector parameterization (CVP), consists in an approximation of the control trajectory by a function of only a few parameters and leaving the state equations in the form of the original ordinary differential equation (ODE) system [Biegler *et al.*, 1999].

In this study, dynamic mathematical model of Catalyzed Esterification of Propionic Anhydride with 2-Butanol is developed to evaluate the concentration profiles of reactants and products during the reaction. The esterification process is simulated in both batch and semi-batch operation. The effect of temperature and feed flowrate (for semi batch) towards conversion and process time are evaluated in the simulation environment. The best of the mode operation chosen is then implemented for the dynamic optimization studies.

2. MODELING OF CATALYZED ESTERIFICATION

2.1 Reaction Kinetics

Esterification of propionic anhydride with 2-butanol produce sec-butyl propionate and propionic acid. In fact, this esterification reaction scheme is more complex, and involves a reaction between the side product propionic acid and 2-butanol to form the same ester and water. The water then can hydrolyze some of the propionic anhydride. However, the reaction rate between propionic acid and 2-butanol is negligible when propionic anhydride is present [Wilder and Karlsson, 2006]. This homogeneous reaction is moderately exothermic with no danger of decomposition reactions. The reaction rate variable is a function of catalyst (strong acid, such as sulphuric acid); exhibits a second-order kinetics when no strong acid is present and exhibits a kind of autocatalytic behaviour when sulphuric acid is introduced [Ubrich, et al., 1999].

In the presence of sulfuric acid, Zaldivar et al. [1993] found that the reaction rate seems to be proportional to the acid concentration; the reaction rate increases with propionic acid concentration and lead to a kind of autocatalytic behavior. However, after reaching a certain concentration, propionic acid has no longer influenced the reaction rate. Since the various theoretical reaction pathways are complex, a model was developed by assuming the existence of two catalysts (cat1, cat2) [Dhanuka, Malshe, & Chandala, 1977]. Meanwhile, the transformation of the initial catalyst was developed by taking into account the acidity function [Benaissa et al., 2008]

The esterification reaction scheme under consideration can be written as:

- Reaction 1: 2-butanol + propionic anhydride \rightarrow propionic acid + sec-butyl propionate
- Reaction 2: catalyst 1 \rightarrow catalyst 2.

The reaction rate of the main reaction can be written as:

$$r_1 = (k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B \quad (1)$$

The reaction rate due to the formation of the second catalyst is also taken into account:

$$r_{cat} = k_4 10^{-H} C_{cat1} C_A \quad (2)$$

The expression of the acidity function is:

$$H = -(p_1 C_{cat1} + p_2 C_c) \left(p_3 + \frac{p_4}{T} \right) \quad (3)$$

Equations (1) – (3) are taken from Zaldivar et al. [1993]

Reaction rate constants follow Arrhenius law:

$$k_i = k_{oi} \exp\left(\frac{E_{ai}}{RT}\right) \quad (4)$$

The kinetic parameters used in this work are tabulated in Table 1.

Table 1: Kinetic parameter equations [Zalvidar et al, 1993]

Subscript <i>i</i>	k_{oi}	E_{ai} (J mol ⁻¹)	Parameter p_i
1	5.36178×10^7 L mol ⁻¹ s ⁻¹	80,478.64	2.002×10^{-1}
2	2.8074×10^{10} L ² mol ⁻² s ⁻¹	79,159.5	3.205×10^{-2}
3	3.9480×10^{10} L mol ⁻¹ s ⁻¹	69,974.6	-21.3754
4	1.4031×10^8 L mol ⁻¹ s ⁻¹	76,6172.2	12706

2.1 Mass balance of batch and semi batch reactors

The mass balances are developed according to the following assumptions: constant reacting heat capacity, effective overall heat transfer coefficient, transport properties of reaction mixture and density are exist; the heat losses with the ambient surroundings are negligible; homogeneous mixing and uniform distribution temperature: no heat accumulation in the reactor wall; no secondary heating effects such as power introduced by stirrer; no pressure effect.

The mass balance of batch esterification reactor:

$$\begin{aligned} \frac{dC_A}{dt} &= -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) \\ \frac{dC_B}{dt} &= -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) \\ \frac{dC_C}{dt} &= ((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) \\ \frac{dC_D}{dt} &= ((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) \\ \frac{dC_{cat1}}{dt} &= -(k_4 10^{-H} C_{cat1} C_A) \end{aligned} \quad (5)$$

The mass balance of semi batch esterification reactor:

$$\begin{aligned}
 \frac{dC_A}{dt} &= -((k_1 + k_2 C_{cat1})C_A C_B + k_3 C_{cat2} C_B) + \frac{F_o}{V} (C_{A0} - C_A) \\
 \frac{dC_B}{dt} &= -((k_1 + k_2 C_{cat1})C_A C_B + k_3 C_{cat2} C_B) - \frac{F_o C_B}{V} \\
 \frac{dC_C}{dt} &= ((k_1 + k_2 C_{cat1})C_A C_B + k_3 C_{cat2} C_B) - \frac{F_o C_C}{V} \\
 \frac{dC_D}{dt} &= ((k_1 + k_2 C_{cat1})C_A C_B + k_3 C_{cat2} C_B) - \frac{F_o C_D}{V} \\
 \frac{dC_{cat1}}{dt} &= -(k_4 10^{-H} C_{cat1} C_A) - \frac{F_o C_{cat1}}{V} \\
 \frac{dV}{dt} &= F_o
 \end{aligned} \tag{6}$$

Where F_o is the feed rate.

3. SIMULATION STUDY OF ESTERIFICATION REACTOR

In this study, 2 variables i.e. feed rate (only for semi batch) and temperature are varied to generate 93- 97% conversion [Andre' et al., 2002]. There were 8 runs of different feed rate were simulated: runs 1-4 used dynamic feed rates; runs 5-8 used constant feed rates. The best feed rate obtained would be implemented to study the effect of temperature in the semi batch operation. The effect of temperature was conducted by varying its value in the range of 303 K to 343 K. This range of temperature was chosen because it can lead the catalyzed esterification process react completely [Zalvidar et al., 1993]. The initial concentration for reactants used for both modes were same, i.e, 1 M which was the adequate condition for comparative performance studies [Ubrich et al, 1999]. Total volume solution applied for both operations was 2 L. The runs conducted in this study are tabulated in the Table 2.

4. DYNAMIC OPTIMIZATION STUDY

In this work, vector parameterization (CVP) was implemented within MATLAB environment by using *DOTcvp* code package created by Hirmajer et al. (2010). The basis of the CVP method is to parameterize the control trajectories and leave the state trajectories continuous. First, the ODE solver calculates the differential equation. Then, the original problem of dynamic optimization is transformed into the finite dimensional problem (NLP) for execution the static optimizer. Further, a suitable gradient method with a NLP type algorithm is needed. This corresponds to a 'feasible' path approach since the differential equations are satisfied at each step of the optimization. A piecewise-constant or piecewise - polynomial approximation of the inputs is often utilized. The general problem of the dynamic optimization can be expressed by applying the combination of the objective function, the equality and the inequality constraints as well as bounds of the model. The basic procedure followed is:

- 1) Parameterize the inputs using a finite number of decision variables (typically piecewise polynomials). The vector of decision variables also includes final time.
- 2) Choose an initial guess for the decision variables.

- 3) Integrate the system states to the final time and compute the performance index and the constraints.
- 4) Use an optimization algorithm (such as steepest descent or Quasi-Newton methods) to update the values of the decision variables. Repeat Steps 3-4 until the objective function is minimized.

The reactant and product concentration are considered as state variables. There were two optimization problems considered in this study. The objective of both problems (problem 1 and problem 2) is to minimize process time to achieve 97% conversion in semi batch reactor. The control variable for problem 1 is feed rate, while for problem 2 are feed rate and temperature reactor. The inequality constraint associated for both of two problems is a total volume solution; whereas the equality constraint is conversion. The fixed time interval used is 10 of piece wise constant. The dynamic optimization formulations for both problems are shown as:

Problem 1

$$\min_{u(t)} \mathfrak{J} = t$$

subject to semi batch dynamic model:Eq.6

$$\text{inequality constraint: } V \leq 2L$$

$$\text{equality constraint: } \frac{C_{B0} - C_B}{C_{B0}} = 0.97$$

$$\text{bounds: } 0 \leq Fo \leq 3 \times 10^{-4} L/s$$

Problem 2

$$\min_{u(t)} \mathfrak{J} = t$$

subject to semi batch dynamic model:Eq.6

$$\text{inequality constraint: } V \leq 2L$$

$$\text{equality constraint: } \frac{C_{B0} - C_B}{C_{B0}} = 0.97$$

bounds:

$$0 \leq Fo \leq 3 \times 10^{-4} L/s$$

$$303^0 K \leq T \leq 343^0 K$$

Table 2. Various Types of Runs in the Simulation Study

Run	Type of operation	Temperature (K)	Feed rate (L/s)
1	Semi batch	323	Dynamic 1.43x 10 ⁻⁸
2	Semi batch	323	Dynamic 1.68x 10 ⁻⁸
3	Semi batch	323	Dynamic 3.77x 10 ⁻⁸
4	Semi batch	323	Dynamic 1.47x 10 ⁻⁷
5	Semi batch	323	Constant 8.46x 10 ⁻⁵
6	Semi batch	323	Constant 9.26 x10 ⁻⁵
7	Semi batch	323	Constant 1.38 x10 ⁻⁴
8	Semi batch	323	Constant 2.78 x10 ⁻⁴
9	Batch	323	-
10	Semi batch	303	Optimum feed rate
11	Semi batch	313	Optimum feed rate
12	Semi batch	323	Optimum feed rate
13	Semi batch	333	Optimum feed rate
14	Semi batch	343	Optimum feed rate
15	Batch	303	-
16	Batch	313	-
17	Batch	323	-
18	Batch	333	-
19	Batch	343	-

5. RESULTS AND DISCUSSION

5.1 Effect of feed rate

The simulation results of 9 runs are tabulated in Table 3. While the conversion for runs 1, 5 and 9 are illustrated in Figure 1.

Here, all the 9 runs were operated for 197 min. The highest conversion obtained for semi batch was 97% which was obtained from run 1. In figure 1, the gradient of run 1 was lower than run 5. It is indicate that the small amount of concentration that dispersed gradually in the solution provide better contact between feed and initial solution (limiting reactant and catalyst). Moreover, it is also can provide a good mixing which can lead to uniform mixture solution. The good distribution and contact between the reactants and catalyst can enhance the reaction rate thus lead to higher amount of conversion [Shin et al., 1999].

In batch reactor mode of operation, the amount of conversion is very close with the conversion achieved in the semi batch operation. The conversion profile achieved from both operations is also follow the same pattern as can be seen in run 1 and 9 respectively. However, the effect of dilution which influences the contact and distribution among reactants and catalyst may improve the performance of semi batch. Therefore, a feed rate trajectory can be optimized in order to improve the product quality [Zavala et al., 2005, Shin et al., 1999].

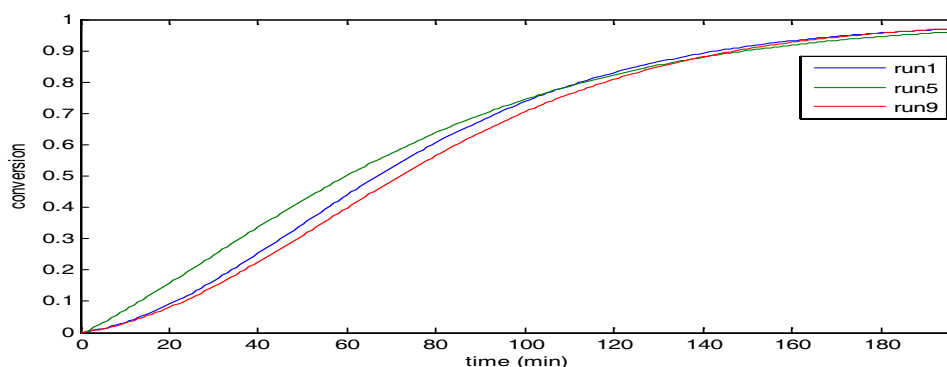


Figure 1: Conversion profile for runs 1, 5 and 9

Table. 3 Final conversion achieved for 9 runs

Runs	Conversion%
1	97.00
2	96.70
3	95.44
4	94.18
5	96.04
6	95.78
7	94.78
8	93.92
9	97.08

5.2 Effect of temperature

The effect temperature in batch and semi batch operation was carried out for temperature range 303 K to 343 K. While, the feed rate applied for semi batch was same as used in run 1. The process time required in achieving 97% conversion for different values of temperatures in batch and semi batch operations is tabulated in Table. 4.

Table.4: Time required for achieving 97% conversion

Runs	Time(min)
10	1154.00
11	463.00
12	197.00
13	87.53
14	40.98
15	1137.00
16	457.65
17	194.98
18	87.43
19	41.06

In Table 4, both modes of operations i.e. batch and semi batch show that the time required for obtaining 97% conversion decrease when the temperature increase. It is because the rates of chemical reactions for reactant, catalyst and product increase exponentially with increase in temperature.

At temperature lower than 323 K, the process time of batch operation is shorter than in the semi batch, but at temperature greater than 333K, process time required by semi batch is shorter than the batch. Thus, it shows that batch operation is superior if slow reaction (longer time operation) is required. Meanwhile if fast reaction is required, then semi batch operation should be selected [Bonvin, 1998]. Moreover, the semi batch operation is preferred to be implemented because it has a good temperature control [Aziz and Mujtaba, 2001]. The feed in semi batch operation is also affected the reaction rate and thus can help to control the temperature. Moreover, the heat produced during reaction can also be controlled by improving the effective heat removing capacity through the feeding reactant. This, in turn, increases the productivity of the reactor by allowing higher reaction rate [Bonvin, 1998].

5.3 Dynamic optimization studies

5.3.1 Optimization of the feed rate (Problem 1)

The optimal feed rate trajectory profile for this problem is shown in Figure 2. To achieve minimum process time for 97% degree of separation, the optimum feed rate trajectory resulted in seven switching times. The switching times occurred at 38, 58, 76, 95, 130, 146 and 168 minute. From Figure 2, it can be observed that the time needed to accomplish the 97% conversion was 186min which shorter than batch process time.

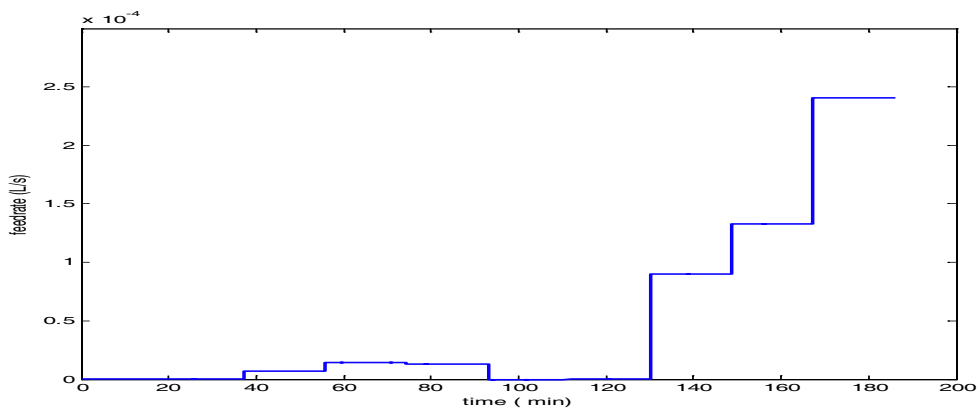


Figure 2: Optimal feed rate trajectory (Problem 1)

5.3.2 Optimization of the feed rate and temperature (Problem 2)

The optimal control trajectories of temperature and feed rate obtained, is shown in Figure 3a and 3b, respectively. The optimum temperature trajectory obtained was changed nine times: at 14, 29, 38, 48, 57, 67, 72, 81 and 93min. On the other hand, optimum feed rate trajectory was switched seven times at 38, 47, 57, 66, 75, 83 and 91 min. The minimum time obtained to achieve 97% conversion is 98 min. The control trajectories obtained are reliable and practical where the time duration to switch between the control values is adequate. However, the change of temperature from one switch to another is not significant. Therefore, only the optimal feed rate trajectory needs to be used for control implementation while the temperature can be kept constant at 331K.

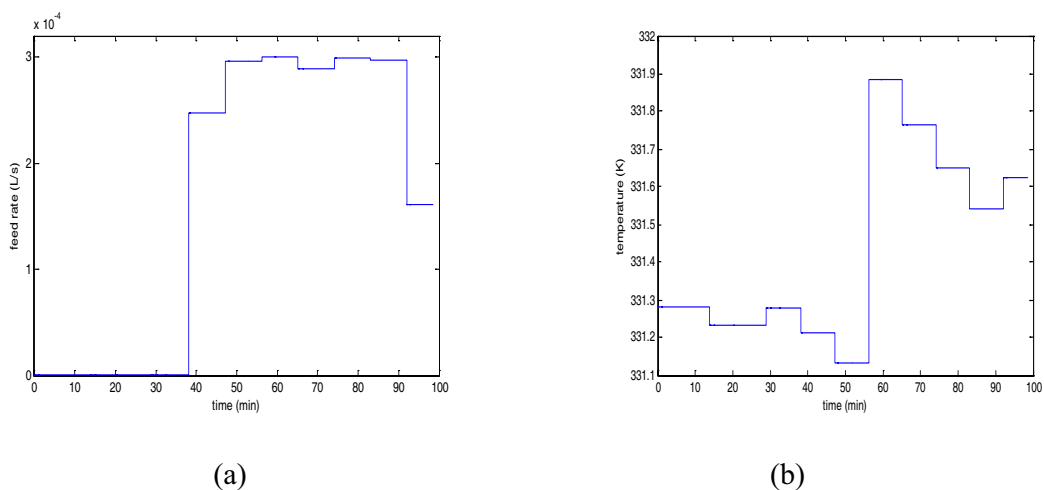


Figure 3: Optimal trajectories (Problem 2): (a) feed rate (b) temperature

6. CONCLUSION

A mathematical model to represent the catalyzed esterification of propionic anhydride with 2-butanol has been developed. A total of 19 runs have been simulated to study effect of feed rate (semi batch) and temperature (both batch and semi batch) towards time required to achieve 97% of conversion. Then the time required to achieve 97% conversion in semi batch operation has been optimized Control Vector Parameterization (CVP) technique. Two optimizations problem have been solved. Both problems aimed to minimize process time in order to achieve 97% conversion. It was observed that the highest conversion can be achieved at the lowest dynamic feed rate. For the effect of temperature, it was found that the process time of batch operation was shorter than in the semi batch when temperature is lower than 323 K, but at temperature greater than 333K, process time required by semi batch is shorter than the batch. For the optimization problem, the optimum temperature and feed rate trajectories obtained were led to shorter process time than batch operation i.e. 98 min in order to achieve 97% conversion. The switching time and the control value obtained in the optimization study were feasible and can be practically implemented. However, the change of temperature from one switch to another was not significant. Therefore, only the optimal feed rate trajectory needs to be used for control implementation.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support by Ministry of Science, Technology and Innovation (MOSTI), Malaysia through the Sciencefund project no. 03-01-55-8F0423.

REFERENCES

1. Andre', R, Bou-Diab, L, Lerena, P, Stoessel, F, Giordano, M, and Mathona, C (2002) A New Reaction Calorimeter for Screening Purposes during Process Development, *Organic Process Research & Development*, **6** : 915-921
2. Aziz, N and Mujtaba, I.M (2001) Optimal control of semi-batch reactors, *European Symposium on Computer Aided Process Engineering – 11*: 609-614
3. Benaissa, W, Gabas, N, Cabassud, M, Carson, D, Elgue, S, Demissy, M, (2008) Evaluation of an intensified continuous heat-exchanger reactor for inherently safer characteristics, *Journal of Loss Prevention in the Process Industries* **21** :528– 536
4. Biegler, L.T., Grossmann, I.E., and Westerburg, A.W. (1999) Systematic methods of chemical engineering process design, *Prentice-Hall PTR*, Upper Saddle River, New Jersey 07458
5. Bonvin, D (1998) Optimal operation of batch reactors view a personal, *Journal of Process Control*, **8**: 355-368
6. Chang, J., and Chen, K. (2004) An integrated strategy for early detection of hazardous states in chemical reactors, *Chemical Engineering Journal*, **98**:199-211.
7. Hirmajer, T, Balsa-Canto, E, and Banga, J.R. (2010) DOTcvp: Dynamic Optimization Toolbox with Control Vector Parameterization approach for handling continuous and mixed-integer dynamic optimization problems, Technical Report.
8. Sauvage, F, (2007) Design and application of state observers for exothermic fed-batch reactors with uncertain kinetics and heat transfer, PhD dissertation, Université catholique de Louvain
9. Shin J, Lee, Y, Park, S (1999) Optimization of the pre-polymerization step of polyethylene terephthalate (PET) production in a semi-batch reactor *Chemical Engineering Journal* **75** : 47-55

10. Srinivasan, B., Palanki, S., and Bonvin, D. (2003) Dynamic optimization of batch processes I. Characterization of nominal solution, *Computers and Chemical Engineering*, **27** (1): 1-26
11. Tsangaris, D.M, and Baltzis, B.C (1996) Evaluation of batch and semi batch reactor operation for enzymatic reactions with inhibitory kinetics *Chemical Engineering Science*, **51**: 2757-2762
12. Ubrich, O, Srinivasan, B, Bonvin, D, Stoessel, F (1999) Optimal Feed Profile for a Second Order Reaction in a Semi-Batch Reactor under Safety Constraints. Experimental Study, *Journal of Loss Prevention in the Process Industries* **12** (6): 485-493
13. Vemuri, Y.J. (2004) Real time optimization of semi-batch reactors, PhD dissertation, Florida State University
14. Widell, R, Karlsson, H.T,(2006) Autocatalytic behaviour in esterification between anhydrides and alcohols, *Thermochimica Acta* 447 57–6
15. Zaldivar, J. M., Hernandez, H., Molga, E., Galvan, I. M., & Panetsos, F. (1993). The use of neural networks for the identification of kinetic functions of complex reactions. In Proceedings of the third European symposium on computer aided process engineering, ESCAPE 3.
16. Zavala, V.M., Flores-Tlacuahuac, A, Vivaldo-Lima, E (2005)Dynamic optimization of a semi-batch reactor for polyurethane production *Chemical Engineering Science* **60**:3061 – 3079
17. Zufferey, B (2006) Scale-down approach: chemical process optimization using reaction calorimetry for the experimental simulation of industrial reactors dynamics, PhD dissertation, Ecole Polytechnique Federale de Lausanne