Match Your Process Constraints Using Dynamic Simulation

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A rigorous dynamic process simulator can be used to evaluate alternative control strategies for an exothermic reacting process in order to improve its safety and product quality.

Like living things, chemical processes are dynamic. Whether they are run continuously, batch-wise or semi-batch, they will exhibit a time-dependent behavior. Steady-state simulation has been a useful tool for the design and rating of single process equipment, as well as for complete plants. Even for day-to-day plant operations, steady-state simulation has been stretched to its maximum by applying it to extract process information and operating conditions that might be evolving with time. However, even with such stretching strategies, steady-state simulation would be of use only for continuously operated processes, not for batch and semi-batch processes.

Dynamic simulation is the tool of choice to reproduce the expected behavior of still-to-be-built plants, as well as to match the operating conditions of already functioning assets. Nevertheless, dynamic simulation has always suffered from a negative reputation, of which the most notable complaints are: a cumbersome tool to use; only accessible to technology gurus; and difficult to economically justify. However, the release of new-generation personal-computer-based dynamic simulators has put at chemical engineers' fingers an easy-to-configure tool that is fast and reliable at a reasonable cost.

The extent of the research literature and the number of textbooks about dynamic simulation topics is vast and the number of theoretical application examples in them is huge, including from single unit operations to plant-wide examples, covering the entire process industry spectrum from oil-and-gas research and exploration to fine chemicals and biochemicals.

Notwithstanding, the immediate advantage that can be anticipated in implementing a dynamic simulation in real plants is the testing and checking of process control strategies. That is the reason why the first process industries that have incorporated dynamic simulation as a common working tool have been the oil-and-gas and refining ones, where controlling and maintaining the productive processes inside a very thin operating interval ensures a continuous flow of on-spec product, crucial aspect of such low added value type of industries.

Recent surveys show that the use of process simulation is growing among the pharmaceutical and fine chemicals industries (/). Typically, these industries use batch processes, dealing with reacting systems where highly exothermic processes are involved. In such scenarios, the thermal behavior of the system has a strong influence on the reaction selectivity and process safety, so the correct control of the process temperature is fundamental. Dynamic simulation enables the engineer to study alternative designs of heat transfer equipment and chemical reactors and, therefore, its use is increasingly expanding inside these high-added-value chemical industries (2).

A dynamic simulation needs the simultaneous solution of algebraic and differential equations, so the proper mathematical algorithms need to be incorporated into a software code. (3–6). Such software has rigorous
models already implemented and the mathematical algorithms ready to use, only requiring the user to enter the relevant chemical information of the process to study. In this context, dynamic simulation becomes an easy-to-use tool, converting the computer into a virtual plant that can be used as a real alternative to expensive pilot-plant studies (7).

This article shows how Hysys, a rigorous dynamic process simulator (3), can be applied to an exothermic reacting process to generate significant improvements in its safety, product quality and productivity. The batch-operated process selected as a case study has been simulated under certain safety constraints. Some alternative configurations of the control system have been designed and tested with the objective to control the process temperature by means of the heating/cooling system or by modifying the dosing rate of the reactants. The flowsheeting capabilities of the dynamic simulator have been used to implement the rest of the upstream and downstream units to cover the entire processing plant. However, for the sake of clarity, the rest of the plant has been removed from the results presented.

Case study overview

The example selected for this study is the esterification reaction of 2-butanol with propionic anhydride. This system has been widely studied in safety assessment because it has two characteristics that make it very interesting (8). First, it is moderately exothermic ($\Delta H_r = -8.0E+04$ kJ/kgmol). Second, the reaction exhibits second-order kinetics when no strong acid is present, and a type of autocatalytic behavior when sulfuric acid is present.

Zaldívar et al. (8), proposed the following empirical kinetic expressions:

$$v_A + v_B \rightarrow v_C + v_D$$  \hspace{1cm} (1)

$$Cat_1 \rightarrow Cat_2$$  \hspace{1cm} (2)

and the following rate expressions:

$$r_B = \left( k_1 C_A + k_2 C_{Cat,1} + k_3 C_{Cat,2} \right) C_B$$  \hspace{1cm} (3)

$$r_{Cat,1} = k_4 10^{-Hr} C_{Cat,2} C_B$$  \hspace{1cm} (4)

where $H_r$ is related to the acidity function and is correlated as:

$$H_r = -(p_1 C_{Cat,1} + p_2 C_{Cat,2})(p_3 + p_4/T_m)$$  \hspace{1cm} (5)

Kinetic constants in Eqs. 3 and 4 follow the Arrhenius equation:

$$k_i = A_i \exp(-E_{ai}/RT)$$  \hspace{1cm} (6)

Table 1 details the values of the $p_i$ parameters in Eq. 5 and the $k_i$ and $E_{ai}$ parameters in Eq. 6.

The process to be simulated will take place in a 3-m$^3$ semi-batch reactor (SBR), stirred at 60 rev/min, working at atmospheric pressure. The heating/cooling system is composed of two service fluids that are fed into a 0.415-m$^3$ jacket on a drain/fill mode. The reactor temperature is the controlled variable according to the control system selected. The utilities used to carry out the process are cooling water at 15°C and heating water at 90°C, with controlled flowrate.

A semi-batch reacting process is an event-driven operating mode for industrial reactors with steps that would be similar to: load reactant A; load catalyst; load reactant B (key reactant); with initial, intermediate or final heating and/or cooling to reach the desired operating conditions.

As planned for the industrial operation, three reacting solutions are used in the simulated experiments: 2-butanol (99% purity), catalyst (70% 2-butanol, 20% sulfuric acid and 10% water) and propionic anhydride (97% purity). The reactor is initially charged with the 2-butanol solution, then during a second step the reactor is charged with the catalyst solution, and finally, the propionic anhydride solution is dosed. All the reactants are fed at 20°C.

The operating procedure and control strategy must satisfy two process constraints — the reactor temperature must not be higher than 60°C and the dosing of the propionic anhydride solution must start once the 2-butanol and catalyst solutions are present within the reactor that will contain a minimum volume equal to 0.4 m$^3$. The process simulator must contain an event scheduler tool that permits the user to implement events on a time- or logic-driven sequence. Be-
cause of this, batch, semi-batch, startups, shutdowns and other plant operations can be easily implemented and simulated. Table 2 shows an example of the event scheduler.

Alternative operating procedures

Four different operating procedures have been tested — isoperibolic, isothermal with feedback control on jacket temperature, isothermal with cascade control on jacket temperature, and isothermal with dosing control — all of them widely used in industrial non-continuous processes. A proposed fifth operating procedure, designed with the objective to optimize batch time and services consumption (and keeping the process inside constraints, mainly to maintain reactor temperature below 60°C) has also been tested.

Obviously, some more traditional advanced control strategies could have been tested. Among others that should be mentioned are:

- The possibility of using three services on the cooling/heating medium for energy conservation.
- The use of non-linear gain on controller configuration to reduce cooling/heating, while reducing overshoot.
- The use of multivariable predictive control technologies. This option is a promising technology that is well-proven in continuous processes, and could be of application in batch systems where a dynamic model could be obtained.

Isoperibolic reactor. The isoperibolic operating mode considers working at a constant temperature for the cooling fluid. This strategy is the most economical because there is no variable controlled along the process, since all parameters are initially fixed. Figure 1 shows the process flow diagram (PFD) for the simulated process plant.

Under this type of operation, the reactor conditions depend strongly on two important process parameters — the temperature of the cooling system and the feed dosing rate of the key reactant. To maximize production, the dosing rate has to be the highest possible one that maintains reactor temperature below 60°C. However, the jacket temperature has to be the lowest possible in order to remove as much reaction heat as possible. Three simulations were run considering an isoperibolic reactor. Figure 2 shows the temperature and mass flow profiles when the cooling fluid enters at 15°C and the key reactant is dosed at a mass flowrate of 1,200 kg/h. The plot shows that in this first try, the process constraint is met for the entire batch time that elapsed 95 minutes in total (batch time includes reactant charging and reaction time, but not product cool-down). Two additional simulations were run, one at a higher jacket temperature (30°C) and the same dosing rate, and another with at a higher dosing rate (2,000 kg/h) and at the same temperature. Although both simulations reduced the batch time, they failed in matching the process constraint.

Figure 2 shows that no accumulation occurs inside the reactor because when the key reactant starts to be dosed, the reactor temperature increases, indicating that the reac-
tion is already activated. Working at the minimum jacket temperature available seems a clear option of choice, but this is not necessarily correct because, in some cases, the reaction rate at low temperatures cannot be high enough to remove the reactant dosed and a dangerous key reactant accumulation occurs. Key reactant accumulation inside an SBR must be avoided because a runaway scenario can easily take place. Since the reaction is already activated and consequently there is no accumulation danger, the conclusion of the isoperibolic tests is to operate the semi-batch plant at a reactor jacket temperature of 15°C.

**Isothermal reactor with simple feedback control.** Isothermal operating mode is based on keeping the reactor media temperature constant during the reaction. This kind of operation is important when secondary reactions can take place because the isothermal process permits the selection of the desired reaction. A first approach to this type of temperature control is to install a simple feedback control loop where the vessel temperature is monitored and the utility valves are manipulated according to the setpoint value. In this operating mode, the propionic anhydride solution is dosed at a constant flowrate only when the setpoint of 60°C is reached after the initial charge of the first two reactants. Figure 3 shows the temperature and mass flow profiles resulting from this simulation.

Three zones can be differentiated in Figure 3. In the first zone, the heating process during the 2-butanol and catalyst feeding, the inlet fluid to the reactor jacket reaches the maximum available temperature of 90°C. When the second zone, the reaction time, begins, the controller has to reduce the jacket temperature due to the release of reaction heat. By the last part of the reaction, the reactor tem-

![Figure 2](image-url)  
**Figure 2.** Temperature profile (left) and mass flow profiles (right) of an isoperibolic reactor when the coolant temperature is 15°C and the mass flow rate of the key reactant is 1,200 kg/h.

![Figure 3](image-url)  
**Figure 3.** Temperature and reactants supply profiles of an isothermal reactor.
perature becomes slightly higher than 60°C; this occurs because the controller has reached its actuation limit since the jacket inlet temperature cannot be lower than 15°C. Therefore, decreasing the dosing rate could be an option to avoid a final temperature deviation, but the process batch time would substantially increase. In a third zone, where the chemical reaction is already finished, there is no heat generation and the setpoint of the controller is already at 60°C, so the heating fluid valve has to be opened again to maintain the reactor temperature.

A longer time (165 min) than in isoperibolic mode is needed to run the process in this way, due to the amount of time required to warm up the reacting mass to 60°C before the key reactant addition starts and to the initial slow dosing rate of the ramp controller.

Isothermal reactor with cascade control. Cascade control is a common control technique that uses two controllers with one feedback loop nested inside the other. The output of the primary controller acts as the setpoint for the secondary controller and the secondary controller controls the final control element (cooling fluid valve).

A different cooling system containing a recycling loop (9) has been implemented in this simulation run as seen in Figure 4. This scheme uses an overflow tank (called T-110) that has been emulated using a level controller, LIC-110, which opens the overflow valve. Another particularity of this configuration is that there is no heating fluid supply, meaning that the fastest way to increase the reactor temperature is to recycle all of the outlet cooling water, which is heated by the reaction heat generated. This operation mode needs 95 minutes to carry out the process.

Isothermal reactor with dosing control. This simulation focuses on regulating the reactor temperature by manipulating the key reactant flowrate, while the jacket inlet temperature is kept constant at 15°C, as the isoperibolic studies suggested.

Figure 5 shows the temperature and mass flow profile for this simulation. Looking at the propionic anhydride curve, it can be seen that the maximum flowrate happens at the beginning of the procedure because the reactor has a lower temperature. The setpoint of 60°C is quickly reached because of the high initial dosing rate. Afterwards, the flow controller has to begin to act by reducing the flowrate. During the rest of the reaction time, the flowrate is slowly increased, compensating the reactants dilution. The operation mode using the dosing control al-

Figure 4. Process flow diagram for simulating isothermal reactor with cascade temperature control.
Figure 5. Temperature profile controlling the dosing flowrate of the key reactant, and reactant supply profile.

Figure 6. Temperature profile controlling the dosing flowrate of the key reactant, and reactant supply profile. A transfer function has been implemented in the flowsheet in order to simulate the thermocouple time response.

Enables the process to be carried out in 83 minutes and provides for more-accurate reactor temperature control.

Isothermal reactor and feeding the reactants as soon as possible. Analyzing the results obtained so far with respect to common industrial procedures, once can conclude that the simultaneous addition of the first reactant and the catalyst would save a minimum of 5 min/run. This is not much time, but if the control system can allow for the simultaneous addition of the three reactants, 20 additional minutes could be saved. Following such a dosing strategy, the reaction would be activated from the very beginning, and at this point in time the reactor would have to be able to remove the generated reaction heat. Normally, this is not possible at the starting time because a minimum liquid level is required inside the reactor for the stirrer to begin to stir the liquid and to have a safe enough heat transfer area. Consequently, when trying this strategy by simulation means, the dosing of the anhydride propionic solution did not start before a minimum liquid volume equal to 0.6 m³ of the other two reactants was already inside the reactor. Moreover, to approach with more fidelity industrial control problems, the thermocouple dead time was included in this simulation. A one-minute delay was incorporated into the temperature signal received by the temperature controller.

Temperature and mass flow profiles can be seen in Figure 6, where a perfect temperature profile is obtained and only 64 min are required to carry out the whole process. It can be noted that the dosing profile shows a remarkable break as a counterpart of the good temperature profile. A smoother controller would have had a more continuous actuation, without such abrupt changes, but then it would have been impossible to avoid an overshoot in temperature profile.

The best way to operate any reacting chemical process is the one that maximizes productivity, subject to applicable process and safety constraints. In the present case study, the dosing control provides the best results, for its rapidity and for the temperature profile obtained. However, in cases where a good accuracy with the thermal behavior is not necessary, an isoperibolic operation could be an option. Nevertheless, isoperibolic operation would require several studies in order to select the best jacket tem-
perature that would allow carrying out the process within the safety and quality requirements. However, in other cases, due to the possible existence of undesired secondary reactions, the temperature control is a fundamental parameter for reaction selectivity; in such situations, an isothermal reaction would be the only way to have the system at the desired working conditions.

The use of dynamic simulation has shown its validity for process development, even in an atypical environment of application like the batch-based chemical industry. Using as process constraints the results obtained in laboratory tests, a simulation model has been developed. The results achieved after several simulation runs have been used in determining an optimal operating procedure (combination of temperature profile and dosing rates) and in ranking some other available non-optimal alternatives. Potentially dangerous pilot-plant experiments have been avoided and sub-optimal control strategies will not be unnecessarily implemented just for testing purposes. As mentioned earlier, cascade temperature control improves the temperature control of the system for faster response. This results in a strong reduction of cycle time over the simple temperature control.

Conclusions
Dynamic simulation usage does not necessarily have to be restricted to some dedicated experts in large corporations. The current existence of powerful and affordable user-friendly packages allows for its utilization not only for operator training systems in already functioning plants, but in the early stages of process development, avoiding the need for sometimes dangerous and expensive pilot-plant experiments. Selecting an optimal control strategy and operating procedure might be a suitable application of dynamic simulation as shown in this article, although the possibilities of the technology are vast and keep expanding. Just to mention a few, the existence of such a virtual plant in a personal computer will substitute the need of a pilot plant in scale-up studies, in batch recipe optimization, in environmental impact assessment studies, in startup/shutdown procedures analysis, and in any other resource-consuming or dangerous activity.

Table 3. Tests summary.

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Conditions</th>
<th>Time, min</th>
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</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>Initial dosing ramp</td>
<td>165</td>
</tr>
<tr>
<td>Cascade control</td>
<td>Dosing at 1,200 kg/h</td>
<td>95</td>
</tr>
<tr>
<td>Dosing control</td>
<td>Tjacket = 15°C</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Dosing at 1,200 kg/h</td>
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Literature Cited