INDUSTRIAL APPLICATION OF PROCESS SYSTEMS TO IMPROVE SPECIALTY BATCH POLYMERISATION PROCESS

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Abstract

There are relatively few industrial applications of process systems to the specialty batch process industry (as compared to bulk continuous or even bulk batch process industry). However, inherent flexibility of these processes can be exploited to increase productivity and product quality. This study is based on a real industrial example of fed-batch polymerisation of ethylene oxide with a base alcohol using an integrated flexible recipe framework. The model parameters of equation based dynamic models have been estimated with real plant data. The objective of the application is to find optimal values for initial variables and controller settings to maximise process profitability. Considerable improvement in process profitability is achieved through a master recipe improvement system (off-line application of the dynamic model). The paper concludes with recommendations to modify conventional practice through the proposed integrated framework.

Keywords

Dynamic modelling, Master recipe improvement, Flexible recipe, Polymerisation reactions.

Introduction

Market dynamics is forcing manufacturing industries to increase productivity and to improve product quality and properties. This is particularly true for batch specialty chemicals as they may take advantage of their inherent process flexibility to achieve this goal.

Batch processes are normally thought to operate at nominal conditions following fixed recipes. Within such operating philosophy, when a recipe is created it becomes an unalterable asset of the company. However, actual commercial process system tools would permit for a better recipe management allowing to enhance batch process profitability in a variety of different production scenarios. Several works refer to the use of flexible recipe management systems in batch process industries (Verwater *et al.*, 1995, Romero *et al.*, 2001).

In the flexible recipe environment, the term recipe is understood in a more abstract way by referring to a selected set of adjustable items that control the process output. Three main levels may be distinguished: (a) The master recipe improvement system, where from accomplished control recipes, recipe models are upgraded and master recipes tuned up, (b) the recipe initialisation level, where different recipe items are adjusted at the beginning of the batch, and (c) the recipe correction level, where the initialised recipe is adjusted to run-time process deviations. The work presented here makes a systemantic application of established process systems tools to focus on a master recipe improvement system of a real industrial scenario of batch specialty products. In the scenario presented, the performance of product recipes is not likely to be well-optimised because of the number of products

concerned and the complexity involved, more likely based on experience of operators. This peculiar aspect has motivated a detailed flexible-recipe study, first developing a comprehensive dynamic model, validated with real plant data, and next integrating it into a master recipe improvement system.

Case Study description

The case study corresponds to the surfactant production of ICI's business *Uniqema* at Wilton, U.K. Specifically the production of one product (P30) in one specific reactor is described in this work. P30 is produced batchwise from the anionic polymerisation of ethylene oxide (EO) with a long-chain base alcohol (R). The polymerisation is carried out in stirred non-flammable closed reactors with internal heat exchangers. Initially, the alcohol is fed to the reactor. After catalyst addition, nitrogen is added to keep non-flammability, reaction temperature is set and monomer addition begins through the bottom of the reactor by means of a sparger. The monomer addition continues until either the desired degree of polymerisation is achieved, the gas mixture in the reactor becomes flammable or maximum pressure is reached. In either situations, the residual monomer is reacted away by stopping feed and maintaining temperature. If reaction is to continue, the reactor is vented to atmospheric pressure, repressurised with nitrogen and monomer feed reestablished.

Process operation conditions of this recipe procedure were determined once, mainly based on a set of company heuristics. However, it is expected that these heuristics do not properly describe the specific reactor behavior, i.e., the fact of being a closed reactor with a liquid volume continuously increasing because of EO 'condensation' on the polymer. Dynamic modelling helps for a better understanding of all the interlinked reactor phenomena.

Dynamic Model description

A simplified scheme of the different processes taking place during reactor operation are shown in Figure 1. The derived detailed model of the polymerisation process describes a nonequilibrium two-phase system with all chemical reactions taking place in the liquid phase. Constitutive equations of this dynamic model are based on the followings,

Component characterisation: The polymer mixture is composed of a distribution of molecules, and the average properties of the distribution changes as the reactions proceeds. One good approach is characterise the polymer using segments. Hence, the initial, end-group and repeated segments are defined and properties are estimated using group contribution techniques. *Polymer plus^{TM}* property packages have been used for these estimations.
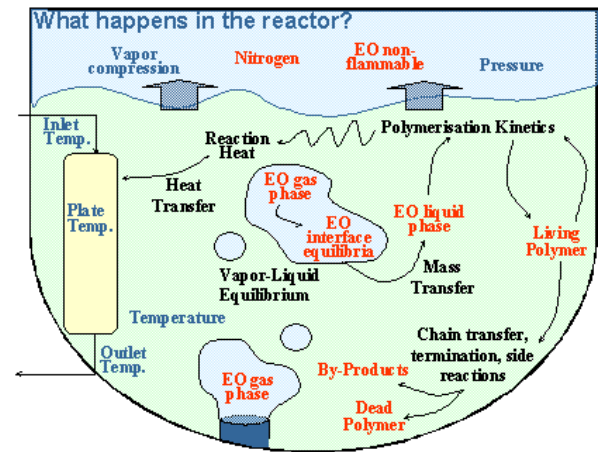

Figure 1. Simplified scheme of reactor behaviour

Kinetic mechanism: Table 1 shows the basic reactions considered in our model. Note that side reactions have been neglected as the objective of this study is just basically describe the recipe behaviour in order to be able to generally improve product performance and not tweaking recipe parameters for sharpen product quality.
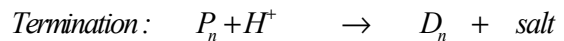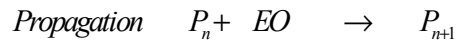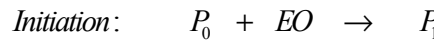
$$Activation: \quad R + NaOH \quad \Leftrightarrow \quad P_0 + H_2O$$
$$Initiation: \quad P_0 + EO \rightarrow P_1$$
$$Propagation \quad P_n + EO \quad \rightarrow \quad P_{n+1}$$
$$Termination: \quad P_n + H^+ \quad \rightarrow \quad D_n + salt$$

Table 1. Kinetic mechanism considered, where R is the base alcohol, P_O the activated carrier, P_1 the initiated chain, P_n the 'live' chains and D_n the dead chains.

Mass transfer of EO from gas phase to liquid phase is considered to be controlling. Equilibrium pressure of EO has been estimated using *Polymer Plus^{TM}* property package POLYUFV (UNIFAC), and corrected with real data adjustment. The overall mass transfer coefficient is defined by the mass transfer coefficient (k_l) and the specific volumetric interfacial area (a). The specific volumetric interfacial area, a, has been considered as a function of EO rate addition. The mass transfer coefficient, k_l, is considered to decrease with viscosity.

Reaction takes place in bulk face according to the kinetics proposed. Heat of reaction is removed by means of internal heat exchanger and liquid enthalpy for energy balance is calculated using *Polymer Plus^{TM}* neglecting vapour enthalpy variations. The global heat transfer coefficient is considered to decrease with liquid viscosity.

As long as reaction takes place, liquid volume increases (as the number of liquid molecules is constant but their molecular weight increases proportionally to the amount of EO added). Hence, during the polymerisation process gas volume is reduced and therefore, as the reactor is closed, partial pressure of nitrogen increased.

The proposed model and different discrete events of the polymerisation recipe have been implemented in *Aspen Custom Modeller[TM]* (ACM). Programmed tasks execute different actions when boundary recipe conditions (end of a batch, gas phase becomes flammable, maximum pressure) are reached.

Model validation

Although some model parameters could be determined from literature sources, it is critical to fine-tune the model with process data, as each specific process has its own particularities that need somehow to be considered in the model. Model parameters to be adjusted are the mass transfer coefficients, polymerisation kinetic coefficients and the global heat transfer coefficient. Two process variables were available for adjustment: pressure and temperature profile in the reactor.. Ideally, each set of parameters described above should be adjusted with a set of independent variable profiles. However, mass transfer and polymerisation kinetics coefficients had to be adjusted vs. pressure and the heat transfer coefficient vs. temperature and heat exchanger profiles.

Figure 2 shows the pressure adjustment. It can be observed how the fitting is quite good but at the beginning of each EO-addition cycle. Here deviations are probably caused by bubble formation dynamics, not contemplated in the actual model. However, to satisfy our objective of globally improve the P30 product performance by means of using a master recipe improvement system, such model accuracy seems to be good enough.
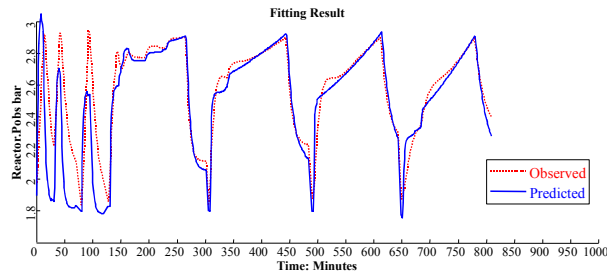

Figure 2. Estimated and real pressure profile

The master recipe improvement system

A master recipe provides information describing how a product is to be produced in a given set of process equipment. From the master recipe, the initial control recipe, the specific recipe to be executed at a given equipment unit, is generated taking into account the plant equipment units, resources and production requirements. During batch operation, this control recipe might be subsequently modified/corrected to give at the end of a batch the accomplished control recipe. The master recipe improvement system uses all of this information for improving recipe models and tuning master recipes. Figure

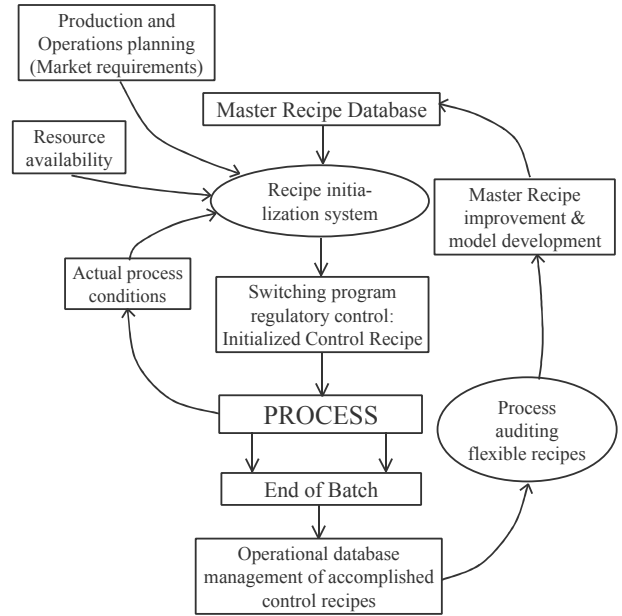3 shows schematically the information flows of such an operating batch system.

Figure 3. Information flow in a master recipe improvement system.

The objective of the master recipe improvement system in itself is to find optimal values for different recipe items. Hence, time varying decision variables, *u(t)*, constant parameters, π, and initial conditions, x_o, have to maximise a product performance function, J (see Eq.2, Abel *et al*., 2000).

$$\max_{u(t),x_o,\boldsymbol{p},t_f} J\big(u(t),x(t),\boldsymbol{p},t_f\big)$$
$$subject\ to,\quad f(x,\dot{x},u,\boldsymbol{p})=0,$$
$$g(x,u,\boldsymbol{p})\le 0, \qquad (2)$$
$$h(x(t_f),u(t_f),\boldsymbol{p})\le 0$$

where x is the system state, f the set of differential and algebraic equations containing the process model and g and h describe the path and endpoint constraints respectively.

In this particular case study, the process model, *f*, is given by the described model implemented in ACM. Batch size and starting pressure of nitrogen are initial time invariant recipe items to be optimised. The monomer feed rate is a time varying item. The end point condition, *h*, is thought to be enough with just consider the desired degree of polymerisation and the path constraints, *g*, are defined by the pressure limit and flammability in the reactor. Product performance, *J*, is defined as the polymer productivity, that is, the end batch size per production span, t_f.

Eq. 2 poses a complex dynamic optimization problem of dificult resolution. In order of effciently solve the problem a set of rationales are considered.Three decision variables describe the optimisation problem established by Eq.2: monomer feed rate (time varying) and initial pressure of nitrogen and batch size (time invariant).

Nitrogen is used as inert diluent to minimise the concentration at which ethylene oxide will propagate a decomposition flame. In principle, the higher the partial pressure of nitrogen used the higher partial pressure of EO is allowed and hence a higher productivity would be expected. However this is not straightforward if consider the reactor is closed besides the factor that at high pressure of nitrogen the limit pressure is quicker achieved. Nonetheless, what is clear is that the reactor is wanted to be operated at the maximum possible pressure the flammability or the pressure limit in the reactor permits.

$$\begin{bmatrix} g(x_{flammability}) = g_{flammabiblity}^{max} \\ g(x_{pressure}) < g_{pressure}^{max} \end{bmatrix} \vee \ g(x_{pressure}) = g_{pressure}^{max} \quad (3)$$

Imposing this disjunctive constraint, the monomer feed rate profile remains fixed and the problem decision variables reduced to initial pressure of nitrogen and batch size. With this, the problem posed by Eq.2 and Eq.3 is solved using a simple non-linear optimisation algorithm. Specifically the Hooke and Jeeves algorithm has been implemented in VBA calling ACM via OLE automation. Within a reasonable number of optimisation iterations, results give that productivity can be increased up to a 34% from the one obtained with the initial master recipe with just one iteration cycle of the operational structure of Figure 3.

Figure 4 shows different optimal pressure and EO feed-rate profiles for different levels of initial reactor pressure for the same batch size. It can be observed how a reduction in N_2 pressure reduces the number of required cookdowns and hence the processing span. Therefore, a reduction in the overall reactor pressure increases productivity. This happens because the lower pressure, the lower compression of nitrogen and, hence, the higuer overall partial pressure of EO. This results are inconsistent with the heuristics used for determining operation conditions of this recipe. Conventional practice of using simple sets of heuristics in recipe development used to be a good aproach when no process insight was possible. However, actual process system tools seem to be able to efficiently deal with these new challenges.

Conclusions

In this work a master recipe improvement system is presented and applied to a batch specialty process. Specifically the polymerisation of a base alcohol is studied. First, a simplified model, based on very first chemical engineering principles, is presented. This basic but complex model has been integrated into a master recipe improvement procedure showing the benefits of using such

an approach when operating the polymerisation batch process case study. The case study presented here also serves to show the potential of systematic process systems application to the specialty batch processing industry and to trigger changes in conventional batch-industrial practice towards the use of these tools.
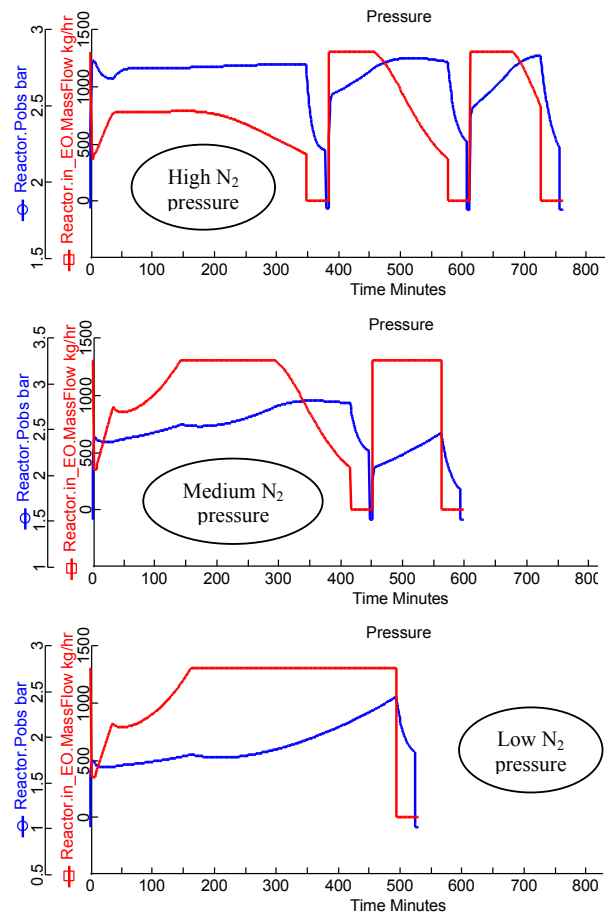

Figure 4. Optimal EO flow rate and Pressure profiles for different initial N_2 pressure.

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