CONSTRUCTIVE NONLINEAR DYNAMICS APPLIED TO DESIGN OF GLYCEROL ETHERIFICATION PROCESS

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O abordare neliniară a proiectării sistemelor de proces este prezentată şi aplicată la instalaţia de obţinere a eterilor de glicerină. Un model matematic simplificat este folosit pentru analiza gradelor de libertate, cu scopul propunerii unei structuri de reglare. În funcţie de parametrii de operare, sistemul prezintă două sau nicio stare staţionară. În prezenţa perturbaţiilor sau incertitudinii parametrilor de operare, varietatea critică ce separă cele două domenii nu trebuie intersectată. Sunt prezentate două metode ce asigură robusteţea sistemului, şi anume analiza neliniară şi o metoda constructivă. Performanţa dinamică este evaluată prin simulare riguroasă în AspenDynamics.

A nonlinear approach to design of process systems is presented and applied to glycerol ethers plant. Based on a simplified mass balance, degree of freedom analysis is used to suggest the plantwide control structure. Depending on the operational parameter, the system shows either two or no steady states. The critical manifold separating the two domains should not be crossed when the system is disturbed or the design parameters are uncertain. Nonlinear analysis and constructive (synthesis-oriented) methods, ensuring the robustness of the design, are presented. The dynamic performance is assessed using rigorous process simulation in Aspen Dynamics.

Keywords: Process design, Constructive nonlinear dynamics, Glycerol ethers

1. Introduction

Many chemical processes exhibit a complex nonlinear behaviour, characterized by undesired phenomena such as state multiplicity, instability, sustained oscillations or domains of unfeasibility ([1], [2], [3], [4]). This undesired behaviour must be taken into account and avoided by proper design and control.

In a typical approach, nonlinear analysis is applied in an iterative manner. The designer starts with an initial design with fixed process structure and

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parameters and then employs established methods (such as bifurcation analysis) to understand the behaviour in parameter space around the nominal operating point. The process understanding accumulated during analysis phase can be effectively used to guide process design ([5],[6]).

However, the methods based on analysis might be very time consuming due to the large numbers of parameters whose influence must be considered and due to large numbers of diagrams that must be drawn. Mönningman and Marquardt ([7], [8], [9]) present a synthesis-oriented method to overcome this limitation.

This paper presents, comparatively, analysis- and synthesis-oriented methods to account for the nonlinear behaviour of a chemical plant. Production of glycerol ethers (Fig. 1) by the reaction of glycerol (G) with isobutene (i-B) is chosen to illustrate the methods. The di- and tri- tert-butyl glycerol ethers (DE, TE) are important for both environmental compliance and efficiency of diesel engines [10]. They are valuable additives due to their anti-detonant and octane-enhancing properties. Moreover, they decrease the cloud point of the fuel and contribute to reduction of fumes, particulates, CO, NOx and carbonyl compounds in engine exhausts [11].

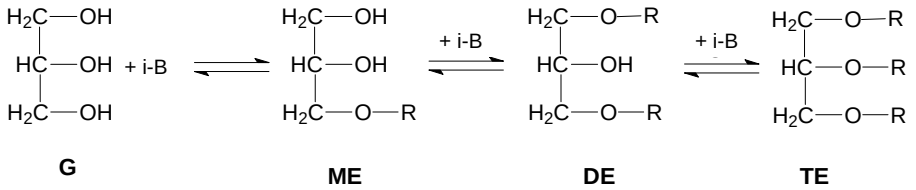

Fig. 1. Etherification of glycerol with isobutene

The paper is organized as follows. The next section considers the reactor-separation-recycle model of the glycerol etherification plant. A simplified mass balance is developed. For the plantwide control structure employed, the system has multiple steady states and the operation becomes unfeasible for large glycerol feed rates or low reaction temperature. Analysis- and synthesis-oriented design methods are applied with the goal of ensuring the feasibility of operation in the presence of disturbances or parameter uncertainty. The performance of the plant is verified by means of rigorous dynamic simulation performed in AspenDynamics. The paper ends with conclusions.

2. Problem formulation

In the following, the design of an etherification plant will be considered. The nominal value of the fresh glycerol feed rate is set to 2 kmol/h, which roughly corresponds to a 15000 tonnes/year biodiesel plant. The design will seek the

minimum volume of a CSTR operated at 363 K. The plant built around this reactor must be able to withstand the increase of the glycerol feed rate to 3 kmol/h and the decrease of reaction temperature to 353 K.

3. The Reactor – Separation - Recycle model

Fig. 2 presents the Reactor – Separation – Recycle structure of the plant. The reactor effluent enters the separation section, where di- and tri-ethers are removed from the plant and two recycle streams are obtained (isobutene, glycerol + ethers). The fresh reactants are mixed with the recycles and fed to the reactor.

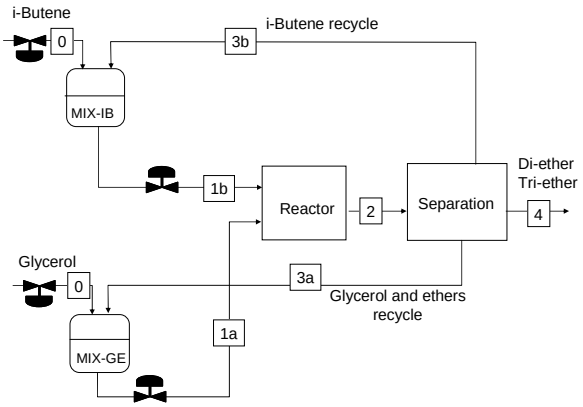

Fig. 2. Reactor - separation – recycle structure of the glycerol etherification plant

A simplified model of the plant [12] is used to investigate the steady state behaviour. The model considers a CSTR operated at a fixed temperature (363 K), where reactions described in Fig. 1 take place (Equation (1)). It is assumed that isobutene, glycerol and mono-ether are recovered from the reactor outlet stream and recycled (Equations (2) to (4)). The make-up of fresh catalyst needed to ensure the reaction conditions was not taken into account. Parameters α and β in equations (5) and (6) account for the fractions of DE and TE recycled from the reactor-outlet. V is the reaction volume. ν is the matrix of stoichiometric coefficients.

$$F_{k,2} - \left(F_{k,1} + V \cdot \sum_{j=1,3} \upsilon_{k,j} \cdot r_j \right) = 0 \qquad k = G, i-B, ME, DE, TE \tag{1}$$

$$F_{G,1} - \left(F_{G,0} + F_{G,2} \right) = 0 \qquad F_{G,4} = 0 \tag{2}$$

$$F_{i-B,1} - \left(F_{i-B,0} + F_{i-B,2} \right) = 0 \qquad F_{i-B,4} = 0 \tag{3}$$

$$F_{ME,1} = F_{ME,2} \qquad F_{ME,4} = 0 \tag{4}$$

$$F_{DE,1} = \alpha \cdot F_{DE,2} \qquad F_{DE,4} = (1-\alpha) \cdot F_{DE,2} \tag{5}$$

$$F_{TE,1} = \beta \cdot F_{DE,2} \qquad F_{TE,4} - (1-\beta) \cdot F_{TE,2} = 0 \tag{6}$$

The reaction rates are calculated by equations (7), where the rate constants follow Arrhenius temperature dependence with parameters taken from [13].

$$\begin{aligned} r_1 &= k_1 \cdot c_{G,2} \cdot c_{i-B,2} - k_{-1} \cdot c_{ME,2} \\ r_2 &= k_2 \cdot c_{ME,2} \cdot c_{i-B,2} - k_{-2} \cdot c_{DE,2} \\ r_3 &= k_3 \cdot c_{DE,2} \cdot c_{i-B,2} - k_{-3} \cdot c_{TE,2} \end{aligned} \tag{7}$$

The concentrations occurring in equations (7) are calculated assuming ideal mixing:

$$c_{k,2} = \frac{F_{k,2}}{\sum_k V_{\mu,k} \cdot F_{k,2}} \qquad k = G, i-B, ME, DE, TE \tag{8}$$

The values used for the molar volume V_μ of glycerol, isobutene, mono-, di- and tri-ethers are (in m^3/kmol): 0.072, 0.094, 0.155, 0.143 and 0.18, respectively.

The model of the glycerol etherification plant consists of 23 equations and contains 25 variables (17 flow rates, 5 concentrations and 3 reaction rates). Therefore, 2 degrees of freedom must be fulfilled through the setting of flowrates by plantwide control (Fig. 3): the flow rate of fresh glycerol, $F_{G,0,}$ and the ratio r_0 between fresh iso-butene and fresh glycerol.

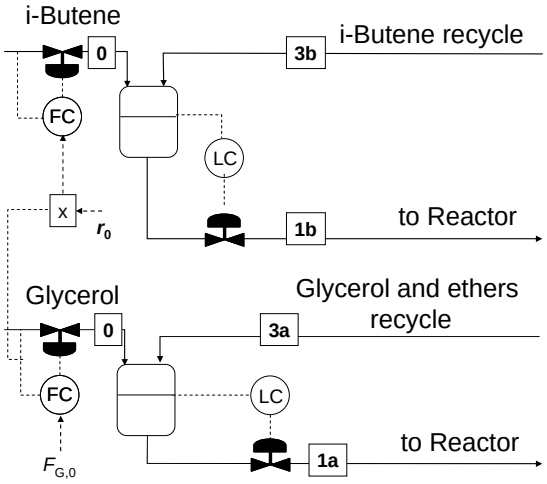

Fig. 3. Setting of the feed rates by the plantwide control

4. Analysis-oriented design method

After the degrees of freedom are specified, the reactor - separation - recycle model can be solved and the dependence of the solution versus model parameters can be traced.

Fig. 4 presents the conversions of glycerol and isobutene (X_G and $X_{i\text{-}B}$, respectively) plotted versus the flow rate of fresh glycerol ($F_{G,0}$). The top diagrams show the variation of conversion for different reactor volumes operated at fixed temperature, T = 363 K. The middle and bottom diagrams show the influence of temperature when the reactor volume is fixed to V=2 m^3 and V = 4 m^3, respectively. All diagrams are plotted for fixed value of isobutene/glycerol feed ratio, $r_0 = F_{i\text{-}B,0} / F_{G,0}$= 2.1. It is assumed that the glycerol and ME recycle does not contain DE and TE ($\alpha = 0$, $\beta = 0$)

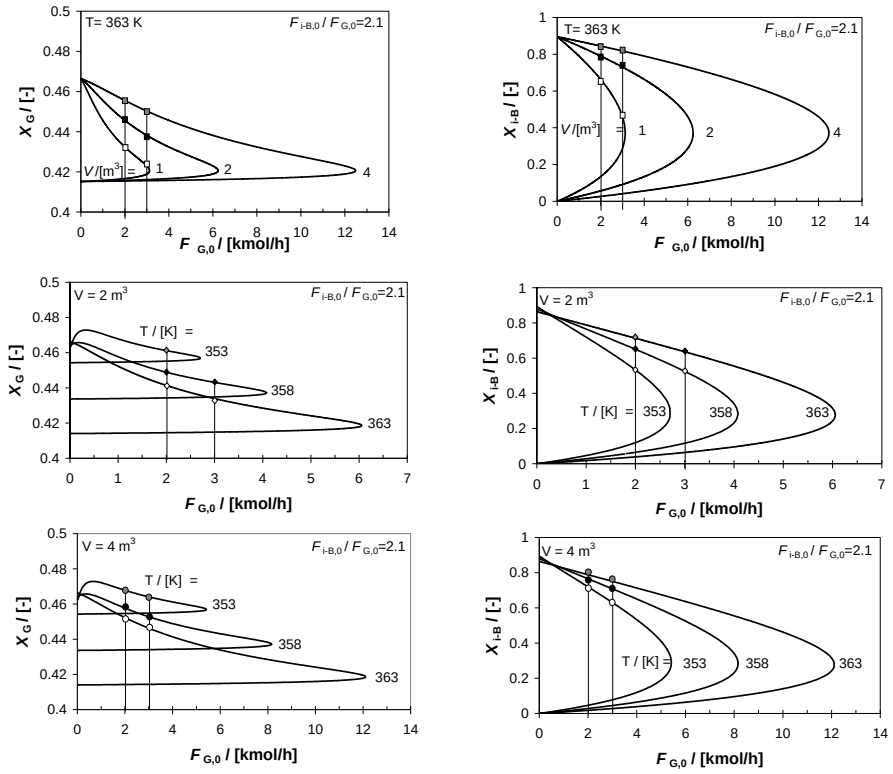

Fig. 4. Results of sensitivity analysis

All the diagram of Fig. 4 are similar: when the fresh glycerol flow rate $F_{G,0}$ is below a certain value (for example, 12.5 kmol/h for a 4 m^3 reactor operated at

363 K, top diagrams), the system shows two steady states. When the feed rate $F_{G,0}$ is increased above this value, no steady state exists. Therefore, the critical value separating the two-state and the zero-state domains represents a feasibility boundary which should not be crossed during operation.

Let us consider a nominal plant capacity $F_{G,0}$ = 2 kmol/h. The top diagrams show that operation is possible using a reactor of 1 m^3 (white square), 2 m^3 (black square) or 4 m^3 (grey square). The plants built around these three reactors will give the same production rate ($F_{G,0}$), although the recycle rates will be different. Moreover, a steady state exists even when the glycerol feed rate is increased by 50% to 3 kmol/h. It should be noted that the operation point of the plant employing the 1 m^3 reactor and processing 3 kmol/h of glycerol is dangerously close to the feasibility boundary, while the 2 m^3 and 4 m^3 reactors are able to handle a substantial increase of fresh glycerol flow rate.

The middle and bottom diagrams of Fig. 4 show the influence of temperature, for the 2 m^3 and 4 m^3 reactors, respectively. For a reactor volume of 2 m^3 and the nominal production rate of 2 kmol/h, an operation point still exists when the temperature is reduced by 10 degrees to 353 K. However, the 2 m^3 reactor can not withstand a feed rate increase from 2 kmol/h to 3 kmol/h combined with a temperature decrease of 10 degrees (nevertheless, a 5 degrees temperature disturbance is allowed).

For the same nominal plant capacity of $F_{G,0}$ = 2 kmol/h, a 4 m^3 reactor can be operated even when the temperature decreases by 10 degrees and the fresh glycerol flow rate simultaneously increases by 1 kmol/h, the new operation point (T = 353 K and $F_{G,0}$ = 3 kmol/h) being far from the unfeasibility domain. Therefore the plant built around the 4 m^3 reactor can be considered safe, being able to withstand large disturbances without crossing the feasibility boundary. However, based on this diagrams, it is rather difficult to predict the minimum reactor volume which allows operation in the presence of these disturbances.

Instead of drawing the conversion versus parameter diagrams, it is possible to directly calculate the boundary between feasibility and unfeasibility, to represent this in the parameter space, and to choose the operating point such that the boundary is not crossed when the process is affected by disturbances.

The feasibility / unfeasibility boundary, located at the turning point of the X_G - $F_{G,0}$ diagrams represent a fold bifurcation of the model (1) - (8). The defining condition of the fold point is [14]:

$$f(x, \delta, p) = 0 \tag{9}$$

$$f_x(x, \delta, p) \cdot v = 0 \tag{10}$$

$$v^T \cdot v - 1 = 0 \tag{11}$$

where

$f(x, \delta, p)$ is a short notation for the model of the plant (eqs (1) -(8))
x is the vector of model unknowns
$f_x(x, \delta, p)$ is the Jacobian of f with respect to unknowns x
$\delta = [T, F_{G,0}]$ is the vector of uncertain parameters
p is the vector of fixed parameters
v is an auxiliary vector having the same dimension as x

The solution of equations (9) - (11) defines the critical manifold (x, δ) having the dimension n_δ - 1 where n_δ is the number of uncertain parameters [9]. This variety can be projected in the n_δ-dimensional space of the uncertain parameters.

In our example, T and $F_{G,0}$ are the uncertain parameters. The critical manifold is one-dimensional and therefore its projection in the two-dimensional T – $F_{G,0}$ space is a line. One such line can be drawn for any value of an additional parameter, for example the reactor volume as shown in Fig. 5.

Each V = constant line divides the T – $F_{G,0}$ plane into two regions. In the right-lower region, two steady states exist and operation of a plant using the reactor of volume V is feasible. In the left-upper region no steady state exists and the operation is unfeasible. The dot shown in Fig. 5 corresponds to nominal operating conditions (363 K and 2 kmol/h). The dashed rectangle represents possible changes of temperature and feed flow rate. It can be observed that, for a 2 m^3 reactor, a simultaneous 1 kmol/h feed rate increase and 10 K temperature decrease renders the operation unfeasible. However, the 3 m^3 reactor appears robust.

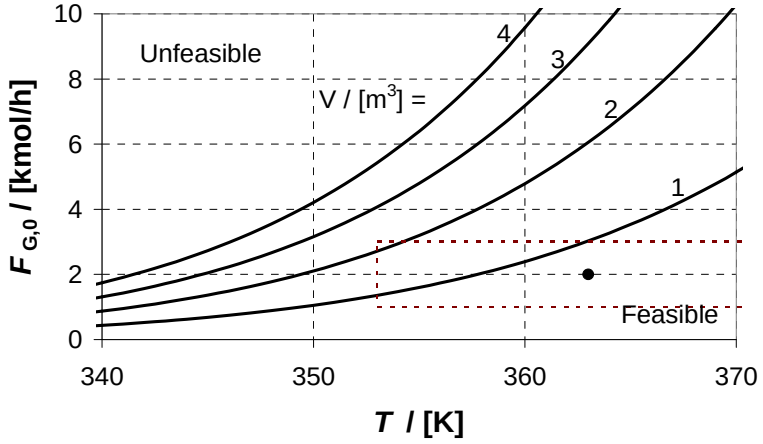

Fig. 5. Projection of the critical manifold into the T - $F_{G,0}$ space

By repeating the calculations in the domain 2 - 3 m^3, a more precise value of the minimum reactor volume could be found.

In theory, the approach outlined in this section could be extended when more varying or uncertain parameters are considered. However, the analysis becomes extremely difficult for two reasons: a) plotting diagrams is restricted to the two-dimensional space; b) the number of diagrams to be traced increases exponentially with the number of parameter [14].

The following section will present a method which can be applied for any number of parameters.

5. Constructive approach

The idea behind the approach presented in the previous section was to place the operating point far enough from the critical manifold, ensuring that this is not crossed when design parameters change or are uncertain. In this section we will give a quantitative definition of the "far enough" condition.

First, we note that the changing parameters are variables with different physical dimensions. Therefore, they can be combined only when they are made compatible by making them dimensionless. Thus we introduce the scaled variables δ_i^s defined by the following equation [14].

$$\delta_i = \delta_i^* + \delta_i^s \cdot \Delta\delta_i \tag{12}$$

where δ_i^* are constants (for example, the nominal value for the parameter i). $\Delta\delta_i$ is the maximum uncertainty or expected change of the parameter *i*. Then, for every scaled parameter *i*,

$$-1 < \delta_i^s < 1 \tag{13}$$

Fig. 6 presents the projection of the critical manifold in the space of scaled uncertain parameters. The origin corresponds to the nominal operating conditions.

In order to quantify the robustness of the operating with respect to changing parameters, we introduce the distance ρ of the nominal operating point δ_0^s to the critical manifold in the subspace of the uncertain parameters. The shortest distance between δ_0^s and the projection of the critical manifold onto the δ-space occurs along the direction *r* that is normal to the critical manifold as shown in Fig. 6. In this figure, the uncertainty box is overestimated by a ball of radius $\sqrt{n_\delta}$. By enforcing the distance ρ between δ_0^s and the critical manifold along the normal direction *r* to be larger than the radius of the ball, the critical manifold is

guaranteed not to be crossed, regardless of the actual values of the uncertain parameters in the robustness box.

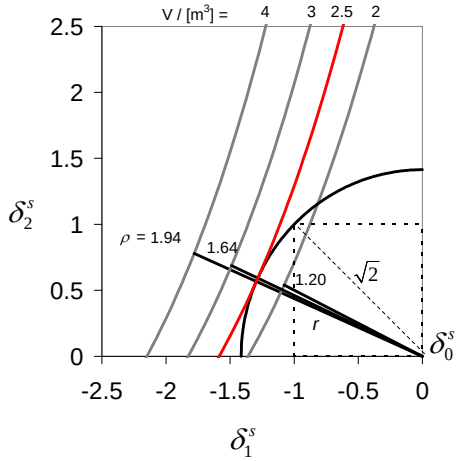

Fig. 6. Projection of the critical manifold into the space of scaled uncertain parameters

The distance ρ between the operating point δ_0^s and the critical manifold can be found by solving the extended system using scaled parameters (15)-(17) together with the additional relationships (18) and (19).

$$f(x,\delta^s,p)=0 \tag{14}$$

$$f_x(x,\delta^s,p)\cdot v=0 \tag{15}$$

$$v^T\cdot v-1=0 \tag{16}$$

$$r-f_{\delta^s}^T\cdot v=0 \tag{17}$$

$$\delta_0^s-\left(\delta^s+\rho\cdot\frac{r}{\|r\|}\right)=0 \tag{18}$$

Finally, an optimization problem can be formulated. In this example we use, for illustration purposes the simple objective function:

$$\min_V V \tag{19}$$

A lower bound of the distance between a candidate point of operation and a critical manifold is imposed:

$$\rho\le\sqrt{n_\alpha} \tag{20}$$

Solving the optimization problem (19) with the equality constraints (14) - (18) and the inequality constraint (20) results in the minimum value of the reactor volume, V = 2.5 m^3, which allows safe operation without crossing the feasibility boundary for 10 K expected change of temperature and for 1 kmol/h expected change of fresh glycerol flow rate (Fig. 6). Therefore the operating point is robust with respect to parameter uncertainty.

6. Dynamic simulation

In this section, the robustness of the constrained-optimization problem result is verified by rigorous dynamic simulation. The plant was designed in AspenPlus [15] around a 2.5 m^3 reactor. Rigorous models for the reactor, L-L separation and distillation column were used. Then, a dynamic model was built in AspenDynamics, where PID controllers were added. Fig. 7 presents results of dynamic simulation. Starting from the nominal steady state ($F_{G,0}$ = 2 kmol/h, T = 363 K), several disturbances were introduced. At time t = 40 h, the flow rate of fresh glycerol was increased to 3 kmol/h. At time 90 h, the reactor temperature was decreased from 363 K (nominal value) to 353 K. In plot a) the molar flows F_{DE} and F_{TE} of di- and tri-ethers in the product stream 4 (Fig. 2) and molar fractions x_{DE} and x_{TE} are presented. In plot b) the flow rate and composition of the reactor-inlet stream 1a is shown, together with the recycle flow rate 3b.

It can be seen that the nominal operating point is stable, and the plant achieves stable operation when disturbances are introduced.

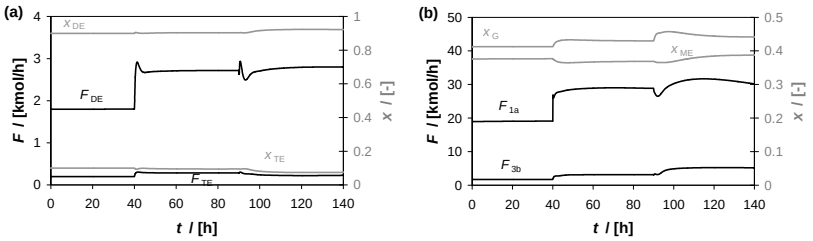

Fig. 7. Dynamics simulation results

7. Conclusions

Chemical processes involving reaction, separation and reactants recycles can have a complex nonlinear behaviour characterized by multiple steady states and regions of operational unfeasibility, as demonstrated for the glycerol - isobutene etherification plant. These phenomena must be addressed during design in order to avoid undesired situations.

Application of methods from field of nonlinear dynamics allows finding an operating point which is robust with respect to disturbances or design parameter uncertainty.

The analysis-oriented method presented in this work is intuitive and can be easily applied. However, it may require a large computation effort and it is limited to a small number of parameters.

The synthesis-oriented method (constructive nonlinear dynamics) does not require drawing of many diagrams and can handle any number of parameters. Moreover, it can be easily integrated within an optimization problem. In this article, the fold bifurcation was considered. However, the method can be extended to other types of critical manifolds.

The effectiveness of the procedure was proved by dynamic simulation.

Acknowledgement

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