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OPTIMAL START-UP AND STEADY-STATE TRANSITION POLICIES IN A PENTENE METATHESIS REACTIVE DISTILLATION COLUMN

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Abstract: The nonlinear analysis and start-up operations of a reactive distillation column were addressed in this paper by approaching the problem as a dynamic optimization problem. A detailed tray by tray model that considers internal tray hydraulics, but ignores vapor dynamics was derived and used for calculations. Several manipulated variables were considered besides the reboiler heat duty. The large scale NLP's generated from the application of the simultaneous dynamic optimization method were successfully solved with the use of Ipopt (an interior point optimizer). It was found that with the use of dynamic optimization large time reductions can be achieved when compared to empirical ramp like changes in the manipulated variables, and, thus, reducing the amount of waste and energy consumption. Overall, when using optimal rather than empirical dynamic operation policies, a one order of magnitude energy and raw material savings where found, which clearly demonstrates that significant economic and environmental advantages can be achieved by approaching the dynamic operation of industrial processes as a formal dynamic optimization problem.

Keywords: Optimal control, reactive distillation, optimal start-up, optimal transition, simultaneous dynamic optimization

1. INTRODUCTION

Reactive distillation (RD) is the process in which vapor-liquid separation and one or more chemical reactions take place simultaneously. In this way only one piece of equipment (reactive distillation column) is used possibly reducing investment and operation costs (Ciric and Gu, 1994). There are several other advantages associated with this process, such as chemical equilibrium limitations can be eliminated, parallel reactions can be reduced, and/or azeotropes can be reacted away (Taylor and Krishna, 2000). Selectivity can be increased by maintaining low concentrations of one of the reactants, thus reducing the reaction rate of parallel reactions. If the reactions taking place are exothermic the heat generated could be used to reduce the reboiler heat requirement. Finally, in packed columns the amount of catalyst required

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may be lowered. Unfortunately, reactive distillation processes have some disadvantages related to the nonlinearities introduced by chemical reaction kinetics coupled with thermodynamic equilibrium relationships. Such nonlinearities could result in the emergence of input/output multiplicities (Ciric and Miao, 1994), and because of this, reactive distillation tends to be a harder process to model, design, and operate. Initial research in reactive distillation focused on single steady state calculations (Holland, 1981), simulation (Ruiz *et al.*, 1995) and dynamic modeling (Taylor and Krishna, 2000). However, recent studies have been done to address the calculation of multiple steady states, process synthesis, and open or closed loop operation.

Compared to the number of publications related to the design, simulation, and control of reactive distillation columns, the number of works devoted to compute optimal start-up trajectories is rather scarce. Ruiz *et al.* (1988) were among the first to use optimization numerical techniques to address the computation of optimal operating policies. Cervantes and Biegler (1998) used the sequential dynamic optimization formulation to minimize the heat required to start a reactive distillation column. Recently Raghunathan *et al.* (2004) formulated and solved a hybrid optimal start-up problem where modeling switches were used to take care of different types of models because of different operating conditions emerging during dynamic transition operations.

In this work the problem of optimal start-up is addressed using dynamic optimization by using the simultaneous approach (Kameswaran and Biegler, 2006).

2. MATHEMATICAL MODEL

The reactive distillation column design was approached using mixed-integer nonlinear and disjunctive programming techniques by Jackson and Grossmann (2001). The tower consists of 27 trays with multiple feeds (trays 12, 13, 17, and 19, numbered from bottom to top) in which the reaction that takes place is the metathesis of 2-pentene to form 2-butene and 3-hexene:

$$2C_5H_{10} \longleftrightarrow C_4H_8 + C_6H_{12} \tag{1}$$

The reaction takes place at atmospheric pressure, and its thermodynamic behavior can be represented with good accuracy using ideal vapor-liquid equilibrium (Reid *et al.*, 1987).

In this section the mathematical model that governs the dynamic behavior of this process is described. The model consists of a tray-by-tray application of the so called MESH equations. They consist in the mass balance (M), thermodynamic equilibrium (E), composition summations (S), and enthalpy balance (H) equations. The modeling assumptions made are: negligible vapor phase dynamics, non-constant molar holdups, liquid hydraulics modeled by the Francis weir equation, thermodynamic equilibrium between phases, a total condenser, and a partial reboiler. The model states are the temperature, the total molar holdup, the individual component holdups, and the liquid and vapor flow rates. Because during start-up operations the concentration of reactants is high all over the column, chemical reaction was considered in all the trays, reboiler, and the condenser. The model used has not been included here because of space limitations, but it can be found in López-Negrete and Flores-Tlacuahuac (2007).

It should be noted that since the model is a system of algebraic and differential equations (DAE) of high index (actually index 2) an index reduction method was applied (Cervantes and Biegler, 1998). Also, the simultaneous dynamic optimization formulation may be consulted elsewhere, for example in Kameswaran and Biegler (2006).

Finally, the objective function used is shown in equation 2.

$$\min \int_0^{\theta} \left\{ \alpha_{\mathbf{z}} \parallel \mathbf{z}(t) - \hat{\mathbf{z}}(t) \parallel^2 + \alpha_{\mathbf{u}} \parallel \mathbf{u}(t) - \hat{\mathbf{u}}(t) \parallel^2 \right\} dt \tag{2}$$

Here θ is the transition horizon, $\mathbf{z}(t)$ is the vector of state variables, $\hat{\mathbf{z}}(t)$ is the vector of desired values for the state variables, $\mathbf{u}(t)$ is the vector of manipulated variables, $\hat{\mathbf{u}}(t)$ is the vector of desired values for the manipulated variables, and $\alpha_{\mathbf{z}}$ and $\alpha_{\mathbf{u}}$ are the objective function weights for the state and manipulated variables respectively.

3. RESULTS AND DISCUSSION

In this section continuation diagrams, start-up operations, and transition trajectories are shown and dicussed. In all cases the feed streams considered are pure pentene at its boiling point with the following values $F_{12} = 36.6$, $F_{13} = 34.3$, $F_{17} = 25$, and $F_{19} = 24$ Kgmol/h. The steady states considered for the start-up, and transition are characterized by the manipulated and output tracking variables values that can be seen in figure 1. Other transitions and start-ups were calculated, but are not shown here because of space limitations (please refer to López-Negrete and Flores-Tlacuahuac (2007)). Although most of the system states were part of the objective function, the

dynamic tracking results are only shown in terms of the two main product streams (i.e., mol fractions and temperature at both the condenser and reboiler). In the first subsection the continuation diagrams are analyzed, ain the second the start-up operation is examined, and in the third the optimal steady state transition is shown. Ipopt (Wächter and Biegler, 2006) was succesfully used to obtain the solutions of the large scale NLP that resulted from applying the SDO formulation for the start-up that was considered.

Nonlinear Analysis Figure 1 shows the nonlinear steady state diagrams of the temperature at the condenser and reboiler (Figs. 1 (a) and (b), respectively) using the reboiler heat duty as the main continuation parameter. The nominal operating point is denoted by the symbol "∘", and the label $ss2$ denotes the steady state used in the optimal start-up calculated (the values of the compositions at the top and bottom products are shown in table 1). The first noticeable aspect of the diagrams is that, around the examined operating region, there are no output multiplicities present and no unstable steady states. An important fact is that at the condenser the nominal operating point is very close to a high sensitivity region. This could bring operating problems if the controller is not properly tuned, for example, if the main continuation parameter is increased to 4×10^6 KJ/h the temperature would increase to 280 K that would represent a decrease of 10% below the nominal value of the composition of the light component. Also, if the heat duty is reduced to 2.5×10^6 KJ/h the temperature of the reboiler would decrease to around 327 K. This represents a reduction of around 20% in the composition of the heavy component in this section of the column. On the other hand, input multiplicities do exist. In the case of the condenser temperature, it can be seen that with a high reflux split fraction (curve 3) input multiplicities exist at low values of the main continuation parameter, and the same is true for the other two values of the reflux split fraction for values of Q_R below the nominal point. This behavior could lead to operating problems if this state is used to track the progress of this process. At the reboiler, the temperature behaves as expected, it increases monotonically with the heat duty until it reaches the boiling temperature of the hexene. Also in the internal trays input multiplicities exist for the compositions of the different components as for the temperatures, these are not shown because of space limitations.

Start-up to steady state 2 In this work the discontinuous step described by Ruiz *et al.* (1988) is not considered, and the model used asumes that the column is filled with some mixture at its boiling point. Ruiz *et al.* (1988) were among the firsts to formulate and solve start-up problems in reactive distillation columns using numerical optimization techniques. The authors used a sequential optimal control procedure. This would require that the DAE system be solved at each iteration of the optimization problem, thus consuming a lot of CPU time. Another problem with this type of formulation could arise if start-up or transitions are done to unstable steady states, because the sequential dynamic optimization method cannot handle them. On the other hand, it has been shown (Flores-Tlacuahuac *et al.*, 2005) that the simultaneous dynamic optimization strategy is well suited to to handle dynamic transitions from and/or to open-loop unstable steady-states.

The initial conditions used during start-up calculations consider that the column is filled with only pentene at its boiling point. Therefore, the individual molar hold-ups are all zero except for the pentene which is calculated from the tray volume (see Jackson and Grossmann (2001)) and the molar density of the pure component. The total molar hold-ups are equal to the individual hold-up of the pentene, and the temperature of each tray is the bubble temperature of the pure component (276.9 K). The reboiler and condenser holdups were 257.9 and 711.23 Kgmol, respectively. Finally, all the internal flow rates (liquid and vapor) are set to zero. The manipulated variables that were used as decision variables to take care of the start-up procedure were: the reflux split fraction (R), reboiler thermal duty (Q_R), opening percentage of the valve that allows the flow of bottoms from the reboiler (β) and the flow rate of each feed stream (F_i). As shown in Eqn 2 all the system states were made part of the objective function and so were the desired values (after start-up is over) of the manipulated variables.

To compare the performance of optimal start-up strategies, the column was also started-up using a heuristic approach. Both the reboiler thermal duty (Q_R) and the flow rate of the feed streams ($F_{12}, F_{13}, F_{17}, F_{18}$) were changed in a ramp-like form. Hence, it was assumed that Q_R changed from its initial start-up value up to its final steady-state value in 7 hr; similarly, all the feed stream flow rates reached their final steady-state values in 2hr. On the other hand, the reflux split fraction (R) and the opening percentage of the bottoms flow rate valve (β) were changed in step-like form.

The optimal start-up profiles for the case in which the set point is steady state 2 are displayed in Figures 2 and 3. The arrowheads on each curve show which y-axis to use to read them, and, as usual, the lower x-axis is used with the left y-axis. Therefore, the upper x-axis is to be used with the right y-axis. In this case a large reduc-

Table 1. Temperatures (T) and compositions ($x_{C_5}, x_{C_4}, x_{C_6}$) at the condenser and reboiler at each of the analized steady states; (1) nominal and (2) $ss2$.

Variable/Steady State	1	2	Variable/Steady State	1	2
x_{C_5} at reboiler	0.0187	0.0003	x_{C_5} at condenser	10^{-5}	0.1491
x_{C_4} at reboiler	4.4×10^{-5}	1.5×10^{-8}	x_{C_4} at condenser	0.9999	0.8466
x_{C_6} at reboiler	0.9813	0.9997	x_{C_6} at condenser	10^{-11}	0.0043

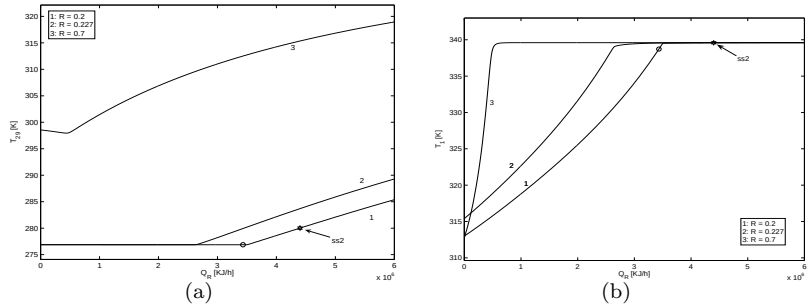

Fig. 1. Continuation diagrams using the reboiler heat duty as the main bifurcation parameter. (a) and (b) stand for condenser and reboiler temperatures. Where ∘ and $ss2$ stand for the nominal and second steady-state.

tion in transition time is shown. For example, the composition of the light component in the condenser (Fig. 2(a)) reaches the steady state at around 5 hours of operation, while the ramp calculation takes far longer than 25 hours. The same can be noticed for the other compositions and the temperature at the condenser. On the other hand, the compositions and temperature at the reboiler take about the same time than the ramp calculation (around 5 hours). This could be explained because the internal liquid hydraulics are modeled, and therefore, a time decoupling effect between the condenser and the reboiler exists. A fast change in the reboiler heat duty (Fig. 3(c)) causes a quick response in the reboiler. This takes a longer time to be displayed in the condenser as in the ramp simulations. In the calculated optimum operating conditions this is countered by quickly increasing the reflux split fraction above the nominal point, thus increasing the amount of mass flowing through in the upper trays and incrementing the heat transfer and temperature of these stages. This is aided by not allowing the flow of bottoms by fixing $\beta = 0$ at the condenser, and by setting high feed flow rates during the first hours of operation. It should be stressed that energy and raw material savings of around one order of magnitude are achieved by using optimal start-up control policies. This can be noticed by evaluating the area below the manipulated variable curves. For example, for the heat duty ramp, this area is equal to 1.0846×10^9 KJ in contrast, the energy consumed for the optimal trajectory is 1.2013×10^8 KJ. The same can be noticed for the feed streams that have overall control energy values of 2.97951×10^4 for the ramp transition and 3.6383×10^3 for the optimal transiton.

Transition 1 ⇒ 2 Figure 4 shows the response of the column for the transition from steady state 2 to 1 (nominal). For this case, the only manipulated variable considered was the reboiler heat duty. Here, Fig. 4(a) is the mole fraction of the light component, (b) is the mole fraction of the heavy component, (c) is the temperatures of the condenser and reboiler, and finally (d) is the reboiler heat duty. It can be noticed that the condenser takes less time than the reboiler to complete the change. This could be explained by looking at the reboiler heat duty (Fig. 4(d)) which is decreased at first causing a lower flow rate of vapor to the top of the column. Since vapor dynamics are not modeled, this change passes through the rest of the trays very quickly, lowering the condenser temperature fast, thus reaching the set point. On the other hand, the reboiler, that is full of liquid, takes longer to reach its set point, because the increase in the manipulated variable is done slowly. It takes almost 40 hours for it to reach its nominal value. The ramp change simulation is barely visible because it takes almost 10 times longer to reach the set point than the optimal trajectory. For example, in figure 4(c) a dashed almost horizontal line can be seen at a temperature of 339.5 K which corresponds to the ramp dynamic simulation. It looks straight because it has a very small negative slope, and it will eventually reach the desired set point. It should be pointed out that significant energy savings can be achieved by using optimal control policies rather than empirical ones. The control energy of the reboiler heat duty for the ramp transition is 1.7182×10^9 KJ, while for the optimal trajectory is 1.8392×10^8 KJ. In fact, the difference is of almost one order of magnitude.

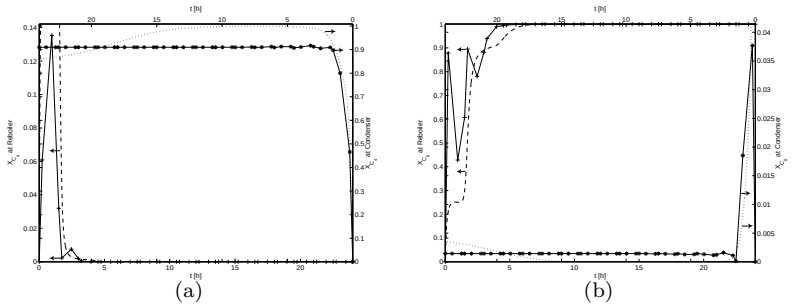

Fig. 2. Optimal start-up transition to steady state 2. Reboiler: $--$ = ramp dynamic simulation, $-+-$ = optimal transition trajectory. Condenser: $-\cdot-$ = ramp dynamic simulation, $-\bullet-$ = optimal transition trajectory.

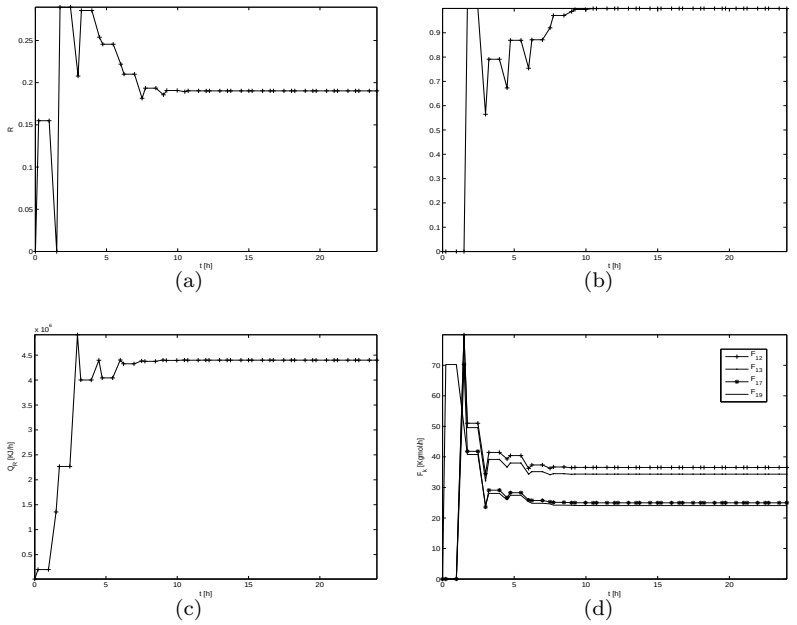

Fig. 3. Manipulated variables for start-up to steady state 2.

4. CONCLUSIONS

In this paper the nonlinear analysis, the optimal start-up, and the optimal set-point transition of a reactive distillation column was done. The optimal trajectories were addressed by using the simultaneous dynamic optimization approach for solving optimal control problems. It was shown that with the use of this technique it is possible to reduce operating times when compared to empirical start-up policies. It is also shown that optimal manipulated variable trajectories are not just simple step/ramp changes, and in reality, because of the nonlinear nature of the process, they are some times not obvious.

The nominal operating steady state is located in an area where small changes in the manipulated variable may cause large changes in the column response. Therefore, if controllers are used they should be well tuned in order to avoid operating problems. In future works this could be addressed by the use of simultaneous design and control, where during the design stages the nonlinear nature of the process and the dynamic behavior are taken into consideration.

For the addressed case study, it has been demonstrated that significant energy and raw material savings could be achieved by using optimal control strategies instead of those based on empirical ones. In fact, the energy difference between optimal and empirical operating policies could be as large as one order of magnitude. Similar savings in raw material consumption were also observed. It was also shown that very large scale problems can be solved with the use of Ipopt.

Future work in the area of reactive distillation is aimed to address the following issues: (a) To consider simultaneous design and control as a way to achieve economical design with operability characteristics, (b) To use different kinds of models during the start-up period by approaching the problem as a hybrid dynamic optimization problem, (c) To get optimal operating policies for

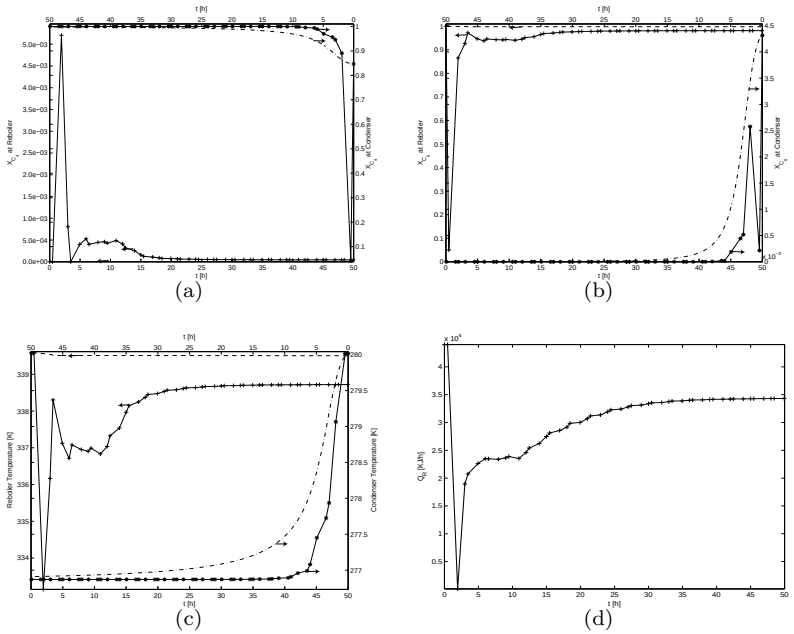

Fig. 4. Compositions (a, b), temperature (c), and reboiler heat duty (d) dynamic response during transition from steady-state 2 to steady-state 1. Reboiler: $--$ = ramp dynamic simulation, $-+-$ = optimal transition trajectory. Condenser: $-\cdot-$ = ramp dynamic simulation, $-\bullet-$ = optimal transition trajectory.

more complex distillation configurations (i.e., heat integrated columns) and (d) To test the validity of the optimal operating policies by implementing them in pilot plant scale experimental equipment.

REFERENCES

Cervantes, Arturo M. and Lorenz T. Biegler (1998). Large-Scale DAE Optimization Using a Simultaneous NLP Formulation. *AIChE J.* **44**(5), 1038–1050.

Ciric, Amy and Deyao Gu (1994). Synthesis on Nonequilibrium Reactive Distillation Processes by MINLP Optimization. *AIChE J.* **40**(9), 1479–1487.

Ciric, Amy and Peizhi Miao (1994). Steady State Multiplicities in an Ethylene Glycol Reactive Distillation Column. *Ind. Eng. Chem. Res.* **33**, 2738–2738.

Flores-Tlacuahuac, Antonio, Lorenz T. Biegler and Enrique Saldívar-Guerra (2005). Dynamic Optimization of HIPS Open-Loop Unstable Polymerization Reactors. *Ind. Eng. Chem. Res.* **44**(8), 2659–2674.

Holland, Charles D. (1981). *Fundaments of Multicomponent Distillation*. McGraw-Hill. USA.

Jackson, Jennifer R. and Ignacio E. Grossmann (2001). A Disjunctive Programming Approach for the Optimal Design of Reactive Distillation Columns. *Comput. Chem. Eng.* **25**, 1661–1673.

Kameswaran, Shivakumar and Lorenz T. Biegler (2006). Simultaneous Dynamic Optimization Strategies: Recent Advances and Challenges. Accepted for publication in *CPC7*.

López-Negrete, Rodrigo and Antonio Flores-Tlacuahuac (2007). Optimal Operating Policies of a Reactive Distillation Column. *Ind. Eng. Chem. Res.*

Raghunathan, Arvind U., M. Soledad Diaz and Lorenz T. Biegler (2004). An MPEC Formulation for Dynamic Optimization of Distillation Operations. *Comput. Chem. Eng.* **28**, 2037–2052.

Reid, Robert C., John M. Prausnitz and Bruce E. Polling (1987). *The Properties of Gases and Liquids*. 4th ed.. McGraw-Hill Companies. USA.

Ruiz, Carlos A., I. T. Cameron and R. Gani (1988). A Generalized Dynamic Model for Distillation Columns–III. Study of Startup Operations. *Comput. Chem. Eng.* **12**(1), 1–14.

Ruiz, Carlos A., Marta S. Basualdo and Nicolás J. Scenna (1995). Reactive Distillation Dynamic Simulation. *Trans IChemE* **73, Part A**, 363–378.

Taylor, Ross and Rajamani Krishna (2000). Modelling Reactive Distillation – Review. *Chem. Eng. Sci.* **55**, 5183–5229.

Wächter, A. and L. T. Biegler (2006). On the Implementation of a Primal-Dual Interior Point Filter Line Search Algorithm for Large-Scale Nonlinear Programming. *Mathematical Programming* **106**(1), 25–57.