ROBUST AND EFFICIENT MINLP OPTIMIZATION OF REACTIVE DISTILLATION COLUMNS

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Abstract

In this contribution, the structural and operational optimization of reactive distillation columns by means of mixed-integer non-linear programming (MINLP) techniques is discussed using the synthesis of MTBE as a test case. The discrete character of the structural alternatives and the nonlinear relationships for reaction kinetics, activities, thermodynamic equilibria and economic costs lead to non-convex non-linear problems which usually are hard to solve. The lack of robustness and the unsufficient performance of numerical MINLP solution methods is one of the major obstacles for their application in practice. Here, three steps are presented to improve the robustness and the efficiency of the numerical optimization: 1. The model is implemented in a numerically favorable manner, 2. the algorithmic behavior is improved by means of non-standard solver options and numerical bounds, and 3. an heuristic rule-based initialization scheme is applied.

Keywords

Optimization-based design, Reactive distillation, Mixed-integer nonlinear programming.

Introduction

Reactive distillation is a process which integrates the functionalities of reaction and separation within one apparatus. The integrated reaction separation technique has the potential to decrease the dimensions of the equipment, to increase the degree of heat integration and to overcome chemical and thermodynamical boundaries, such as chemical equilibria or distillation boundaries.

The task to design a reactive distillation column can be formulated as an optimization problem with discrete and continuous degrees of freedom which are fixed subject to linear and nonlinear constraints such that an economic cost function is minimized. MINLP-techniques provide mathematically well-founded methods to model and to solve such problems, but typically they suffer from a lack of robustness and efficiency, which may lead to excessively long computing times and unforeseeable numerical behavior in face of small model changes. In the relevant literature (Ciric and Gu, 1994, Frey and Stichlmair, 2000, Jackson and Grossmann, 2001, Stichlmair and Frey, 2001, Poth et al., 2003) usually only one model instance is considered and data on the numerical performance for variations of the problem formulation is not presented.

In this contribution, the heterogeneously catalyzed and kinetically controlled synthesis of methyl-tertiary-buthyl-ether from isobutene and methanol (MTBE ⇆ IB + MeOH) in the presence of butane at a pressure of 8 bar is considered. The four component mixture exhibits three binary minimum azeotropes (see Table 1, based on Beßling, 1998). The aim is to produce MTBE with a

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purity of 99% from two feed streams (6.375 mol/s MeOH, 8.625 mol/s IB/butane with 65.2% IB, similar to the assumptions in Stichlmair and Frey, 2001) at minimal cost. In the remainder of the paper, the model formulation is sketched and a three-step solution methodology is presented which solves the MINLP problems at hand efficiently and robustly.

Table 1. Boiling points at 8 bar

Components	Temperature [K]
MeOH/IB	332.7
IB	334.5
MeOH/Butane	340.1
Butane	342.5
MeOH/MTBE	393.0
MeOH	401.2
MTBE	409.4

Model Formulation

The model formulation of the tray column follows the common superstructure approach (see, e.g., Jackson and Grossmann, 2001): The superstructure comprises up to 100 trays which may be active or inactive. Active trays have separating functionality and may have reactive functionality, whereby inactive trays have neither. The first and the last tray represent the reboiler and the condenser, respectively, which are always active and non-reactive.

The key variables of the model are: activation of a tray (binary), holdup of a tray (≥0), column diameter (≥0), column height (≥0), vapor and liquid flow rates (≥0), feed streams onto the stages (≥0), bottom and top distillate streams (≥0), molar concentrations and activities (≥0), temperatures [K] (≥0), production rates (≥0), and heating and cooling load of condenser and reboiler (≥0).

Key constraints are: the tray models given by the MESH-equations (material balance, equilibrium condition, summation condition and enthalpy balance), the activity-based reaction kinetics with positive and negative exponents, an extended Arrhenius approach for the kinetic constants, Wilson's approach for the activity-coefficients, the Antoine equation for the vapor pressures, geometric constraints on the vapor velocity and the tray height, the vapor phase Murphree efficiency to reflect the non-ideality of the separating functionality, a purity condition for the bottom distillate stream (MTBE), and empirical correlations for annualized investment costs for the shell, the internals, the reboiler, the condenser and the catalyst, for operating costs for cooling, heating and feed streams, and for the revenues from the bottom and top distillate streams. For further details see Sand et al. (2004).

Specific attention must be paid to the activation concept of a tray k within the superstructure: The separating functionality is controlled by "switching" the Murphree efficiency E_k by means of the binary activation variable φ_k:

$$E_k = 0.7\varphi_k \quad \forall k \tag{1}$$

Additionally, the feed streams to the stages and the holdups are constrained by means of big-M inequalities. Advantages of this approach are that binary variables appear only in a very small subset of the constraints, the binaries enter linearly into the equations, and integer-relaxed values of φ_k are meaningful in terms of the original design problem.

Solution Approach

The MINLP-model is solved by a decomposition-based approach: The integer programming (IP) master-problem is tackled by the branch and bound (B&B) algorithm implemented in SBB (2003), and the NLP-sub-problems are solved by the generalized reduced gradient algorithm implemented in CONOPT (Drud, 2003). (See Sand et al., 2004, for a comparison of the B&B algorithm with enumeration and interval reduction approaches wrt. their theoretical and empirical complexity.) The problem at hand is of minor combinatorial complexity, its numerical difficulty is mainly given by the high, problem-inherent non-linearity of the constraints. The superstructure comprises only 98 different feasible structures, but even with fixed binary degrees of freedom, it is hard to find feasible solutions when using standard algorithmic options and trivial initial values.

The numerical robustness is improved in the following three steps: 1. The model is implemented in a numerically favorable manner. 2. The algorithmic behavior is improved by means of non-standard solver options and numerical bounds. 3. An heuristic rule-based initialization scheme is applied. Each step is evaluated by solving up to 91 MINLP-instances, corresponding to superstructures with 10-100 trays. The robustness is measured by the ratio of optimal (vs. infeasible) solutions and the spread of locally optimal objective values; the efficiency is measured by the CPU-time on a Windows 1,5 GHz PC.

Model Implementation

The model was implemented in GAMS (Brooke et al., 2003) while the rules of thumb from Drud (2003) for numerically favorable formulations were applied carefully: The model was reformulated equivalently by 1. bounding variables to avoid function evaluation errors, 2. implementing only necessary bounds to avoid degeneracy, and 3. introducing auxiliary variables to reduce the complexity and the non-linearity of the constraints.

Examples are: 1. Temperatures were bounded to the spectrum of boiling points from Table 1 to ensure feasibility of the logarithmic temperature differences in the condenser. 2. Molar concentrations were implemented as

non-negative variables, but activities were not bounded (i.e. the implementation allows for negative values) since their non-negativity is implied by Wilson's approach. 3. The Arrhenius approach of the form $e^{-E/(RT)}$ was reformulated by means of an auxiliary variable *aux* to e^{aux}, $aux \cdot T = -E/R$.

For a superstructure with 100 trays this implementation comprises 11,215 continuous variables, 98 binary variables and 11,711 constraints (the size of the model is almost proportional to the number of trays). This model was solved with trivial initial values of 1 for all variables (if 1 is out of bounds for a certain variable the initial value was mapped onto the corresponding bound) and with standard options for CONOPT and SBB. It turned out that **0%** of the cases yielded feasible solutions.

Algorithmic Improvements

The insufficient algorithmic behavior was improved in an iterative manner by 1. setting non-standard CONOPT options and 2. adding numerical bounds based on numerical observations. Since the introduction of binary variables changes the model structure only marginally, the numerical studies could be done with fixed binary variables, i.e. for NLPs, and the results were then used to solve the corresponding MINLPs.

Examples are: 1. Applying Newton's method to find feasible solutions is not appropriate (hundreds of phase 0 iterations without progress, see Drud, 2003), so it is bypassed by introducing slack variables for infeasible constraints (lsslack = 1). 2. In infeasible constraints, the heat load of the reboiler is 0, so a lower bound of 1 kW (which is not active in an optimal solution) is introduced.

This leads to setting non-standard options for the feasibility tolerance (rtnwma = 10^{-6}), the maximal number of stalled iterations (lfstal = 10^5), the optimization of the step size in Newton iterations (lmmxsf = 1) and for the scaling of the variables and the constraints in each iteration step (lfscal = 1), in addition to bounds on the heating and the cooling load, the reflux flow rate, the chemical equilibrium constant, the kinetic constants and various auxiliary variables.

Figure 1 shows the results of 91 MINLP solutions with trivial initial values (see above): The ratio of (feasible) locally optimal solutions **increases from 0% to 97%** with CPU-times of about 1-50 minutes. The majority of the optimal objective values lies on a smooth curve which indicates qualitatively similar solutions, but 34% of the runs end up in local optima which are significantly inferior.

Heuristic Rule-Based Initialization Scheme

To improve the robustness further, an advanced initialization scheme based on heuristic rules is applied. According to the heuristic rules, some variables of the MINLP model are fixed and the objective function is changed. The solution of the resulting NLP-model is then used to initialize the superstructure model described above.

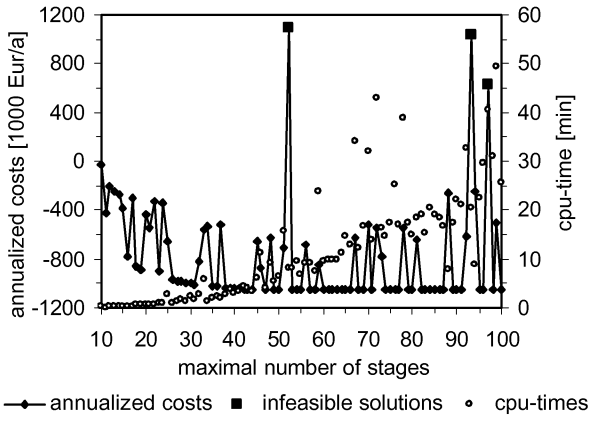

Figure 1. Solutions with trivial initialization

Heuristic Rules

The following heuristic rules (based on experiences and thermodynamic insights) are applied to the process at hand (see Beßling, 1998, Doherty and Malone, 2001):

1. A typical column height is 30 m. 2. If a chemical reaction is necessary, the column must comprise reactive functionality. 3. If the reaction is equilibrium limited and there is only one reaction product and the product should be highly purified then a non-reactive functionality is needed between the reactive functionality and the product port. 4. Expensive separation tasks should be performed within the column. 5. Inhibit the reaction when the composition exceeds the chemical equilibrium composition. 6. If the reactants have very different boiling temperatures then they should be fed separately. The high-boiler feed should be above the low-boiler feed. 6. If the reactants are not needed for the separating functionality then they should be fed onto reactive trays.

Advanced Initialization

According to these rules, the following heuristic bounds, which reduce structural but not operational degrees of freedom, were added to the superstructure model (see Figure 3, left):

1. 38 trays are active, the remainder is inactive. 2. Trays 1-12 and 38 (condenser) are non-reactive, the remainder is reactive. 3. Possible feed trays for IB/butane are trays 13-25 and for MeOH trays 26-37.

Furthermore, the economic objective in the initalization stage is replaced by maximizing the IB-conversion, while the cost correlations remain part of the model.

As before, the algorithmic behavior of the initialization model is improved by bounds (in particular for the column diameter, the holdup and the IB-conversion) and the trivial initialization scheme is applied. The initializa-

tion model comprises the same constraints as the superstructure model thus a feasible solution of the initialization model implies a feasible initialization of the full superstructure model.

Figure 2 shows the results of 63 MINLP runs (superstructures with 38-100 trays) with advanced initial values. 97% of the instances are initialized feasibly, and the ratio of locally optimal solutions increases from 97% to 100%. The robustness of the solutions increases significantly: The ratio of inferior solutions **decreases from 34% to 0%.** The consistency of the CPU-times increases as well, and the maximal CPU-time (including the initialization problem) decreases from 50 to 20 minutes. In the optimal solution 51 trays are active, the column diameter is 0.39 m and the reflux ratio is 4.6. Figure 3 (right) shows the distribution of the functionalities and of the feed trays.

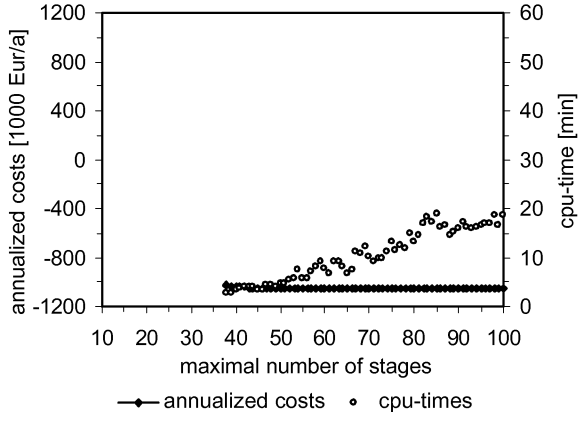

Figure 2. Solutions with advanced initialization

Conclusions

A three-step methodology to solve MINLP models of reactive distillation columns robustly and efficiently was presented. The probability of finding feasible solutions can be increased significantly by means of non-standard solver options and algorithmic bounds, and the robustness and the efficiency of the computations can further be increased significantly by means of an heuristic rule-based initialization scheme. This systematic approach can be applied to similar problems, studies for other reactive distillation problems are under way.

Acknowledgments

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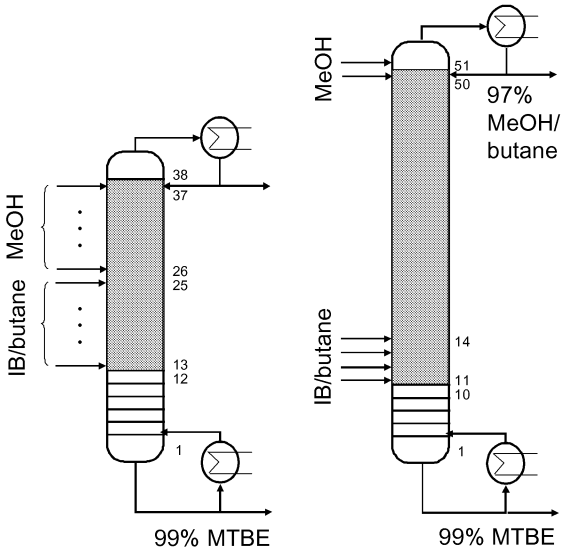

Figure 3. Advanced initialization scheme (left) and optimal solution (right)

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