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Optimal Process Design for the Synthesis of 2,3-Dimethylbutene-1

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Abstract

This paper is concerned with the computer-aided optimal design of reaction-distillation processes. The production of solvent 2,3-dimethylbutene-1 by isomerization of 2,3-dimethylbutene-2 is considered as an innovative benchmark problem. Possible process candidates are a reactive distillation column, a reactor coupled to a nonreactive distillation column or a reactive reboiler with a nonreactive distillation column on top. Local MINLP optimization indicates that the reactive distillation has the lowest total annualized costs. However, due to the non-convexity of the underlying mathematical problem better solutions for the other process candidates cannot be excluded. For this purpose a new global approach is proposed which is based on discrete optimization of the underlying model equations and which proves globally that reactive distillation is the best option.

Keywords: Reactive distillation, isomerization, 2,3-dimethylbutenes, optimization, MINLP

1. Introduction

Reactive distillation combines chemical reaction with distillation within a single processing unit (Sundmacher and Kienle, 2003). Optimal design of such an integrated process can be difficult due to increased complexity. Further, reactive distillation is not the only possibility to combine reaction and separation. Depending on the application to be considered other configurations involving reactors, side-reactors and nonreactive distillation columns can also be attractive (Schönmakers, 2003 and Krishna, 2003). The optimization of the total annualized cost for different alternative processes can provide a suitable platform to determine an overall optimal configuration. However, such an optimization problem is difficult to solve because it includes non linearly connected

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continuous variables and discrete decision variables. For this purpose a new two step optimization strategy is proposed. In a first step, local MINLP optimization methods are applied to obtain a quick preliminary ranking of suitable process candidates (Ciric et al., 1999 and Stichlmair et al., 2001). Afterwards the result is checked by a new global approach. It is based on a discrete relaxation of the underlying mathematical models and leads to an MILP, which can be solved rigorously. In the present case it provides a global lower bound for the cost function of the second best candidate, which can be shown to be always greater than the cost for the first candidate and thereby proves its superiority. As an innovative benchmark problem isomerization of 2,3-dimethylbutene-2 (DMB-2) to 2,3-dimethylbutene-1 (DMB-1) is considered. DMB-1 is a key compound for musk fragrances and insecticides (Sato et al., 1999). The difference in boiling point temperatures of the two isomers is significant, so that reactive distillation seems a suitable option (Kent et al., 1989). In particular, product DMB-1 is the light boiling component.

2. Local Optimizations

Suitable process candidates are shown in Figure 1. These include a reactive distillation column (RDC), a side reactor coupled with a non-reactive column (RPLUSC) and a reactive reboiler with a non-reactive column on top (REACREB). Reactive sections are filled with catalyst. They are indicated by the shaded regions in Figure 1. From the reactive sections the mixture enters a nonreactive separation section, where the light boiling product is enriched and the reactant is recycled back into the reaction zone. The feed positions for RPLUSC and REACREB are fixed at the reactor or the reactive reboiler, respectively. For RDC the feed position and for RPLUSC the position where the reactor effluent enters the non-reactive distillation column are optimization variables. Other optimization variables in all three cases are the amount of catalyst in the reaction section *Mcat*, the reflux ratio *RR* and the total number of column trays *N*. In addition, the number of reactive trays *Nr* is optimized for configuration RDC.

The model equations were obtained from first principles. Because heat effects are negligible, a constant molar overflow equilibrium stage model was used. The vapor liquid equilibrium was modeled with constant relative volatility. The kinetics of the isomerization reaction over Amberlyst 15 catalyst was determined experimentally and is given by the following pseudo-homogeneous rate expression.

$$r_i = \nu_i M_{cat} Kf \left(x_{DMB-2} - \frac{1}{Keq} x_{DMB-1} \right) \tag{1}$$

The physical properties and kinetics parameters are given in Table 1.

Table 1. Kinetics and physical property data

Kf, kmol/kg cat-hr	*Keq*	α
0.1210	0.1070	1.8

The objective function for the optimization was the total annualized cost, consisting of annual capital costs and annual operating costs. The capital costs include cost of equipment, like column shell, column internals, heat exchangers, and reactor. The operating costs include cost of heating and cooling utilities. For details on the model equations and cost functions, readers are referred to Gangadwala et al. (2005).

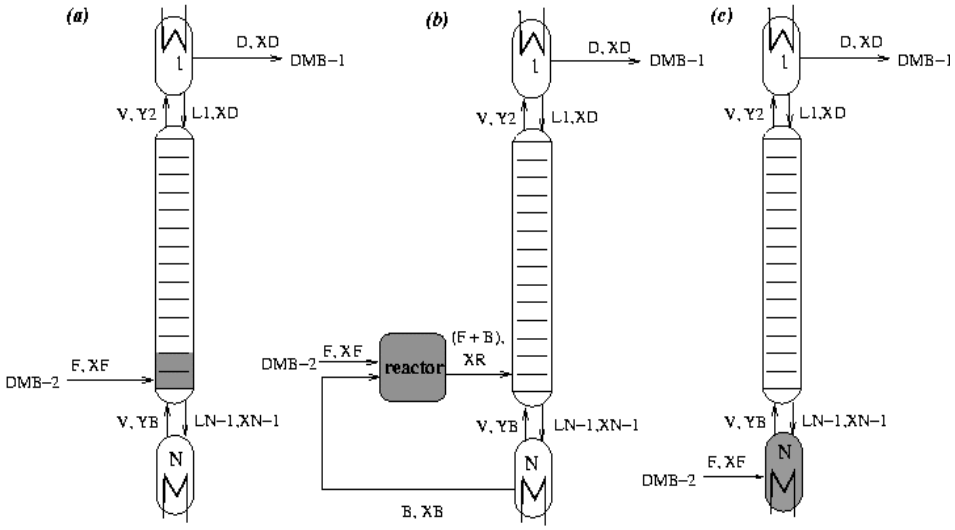

Figure 1. Superstructures: (a) reactive distillation column (RDC), (b) a reactor coupled with distillation column (RPLUSC), and (c) distillation column with reactive reboiler (REACREB)

The resulting MINLP problems were solved using standard optimization tools in GAMS (Brooke et al., 1998). In particular the branch and bound method SBB was used with CONOPT for the NLP subproblems and CPLEX for the MIP subproblems. The upper bound on the total number of stages was set rather high at 60. A minimum product purity of 99.2 % of DMB-1 in the distillate was required. For a pure DMB-2 feed and a feed flow rate of 1.4852 kmol/hr, the local optimization results in Table 2 suggest a ranking of all three process types. W. r. t. the first two processes, RDC and RPLUSC, the ranking is non-conclusive, while the process REACREB is clearly not a competitor. However, due to the nonlinearity of the problems considered only local optima can be obtained and no guarantee for the globality of the optimal solutions can be given.

Table 2. Comparison of locally optimal total cost

	Total cost	*Capital cost*	*Operating cost*	*Mcat*	*RR*	*N*	*Nr*	*FTL*
RDC	183000	120000	63000	76.09	13.99	24	20-23	23rd
RPLUSC*	187000	115000	72000	197.13	16.06	22	-	20th
RECREB	302000	162000	140000	42.52	32.51	21	21st	21st

* optimal value for the bottoms flow rate B is 69.71 kmol/hr

3. Global Optimization

The results in the previous section show that the minimal annual total cost of the local optimal solution for the RDC and RPLUSC process hardly differ from each other, while the cost of the local optimal solution for the REACREB is significantly higher. The objective of this section is to prove with methods from discrete mathematics that the RDC process is the superior process from an economic point of view. In order to achieve this a mixed integer linear program is constructed in such a way that its solution set contains all feasible solutions of the RPLUSC process. The optimal value of its objective function provides a global lower bound of the total cost of the RPLUSC process. Indeed by using nontrivial algorithmic techniques in combination with severe computational testing, one can show that the optimal value of the constructed mixed integer linear program is greater than the cost of the known solution of the RDC process in Table 2. From the theory of mixed integer linear programming it then follows that the RPLUSC process cannot work with less annual total cost than the RDC process. We note that mixed integer linear programs can today be solved using software employing simplex-based branch-and-cut algorithms.

To construct such a mixed integer linear model each nonlinear term in the original non-linear model is approximated by an enclosing polyhedral relaxation. This procedure can best be understood when looking at the function $f : R \rightarrow R$, $f(x) = \dfrac{\alpha \cdot x}{1 + (\alpha - 1) \cdot x}$ which appears in the vapor liquid equilibrium equations. The function is monotonuously increasing and concave for $x \in [0,1]$ and $\alpha \geq 1$. The graph of f can be linearly approximated on any subinterval of [0,1] by the tangents and the secant of the interval boundaries, see Figure 2.

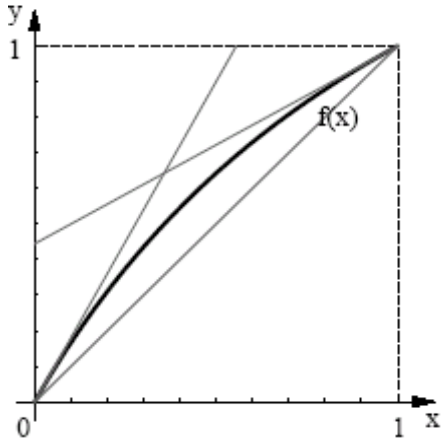

Figure 2. Polyhedral approximation of a non-linear function.

Functions which are not monotonous or convex can still be approximated in a likewise fashion by adaptively decomposing their domain and computing approximations for each region separately. Then, using binary variables to index the components of the decomposition, the individual polyhedral approximations can be united in a single

mixed integer linear program. In the model for the RPLUSC process, this is done for all the nonlinear terms in the component material balances, vapor liquid equilibria, and for the objective function. The domain is decomposed into a collection of cubes, allowing us to increase the strength of the approximation by decreasing the size of the cubes, at the expense of a larger model formulation.

By the above method we construct a family of mixed integer linear programs where the number of stages N and the feed-position can be freely chosen. We solve these problems for each fixed N to a reasonable size, and each fixed feed-position in $[2,N-1]$. Some of the resulting problem instances (for a low number of stages or obviously very bad feed position) can be solved immediately, while most had to be decomposed further by splitting the domain of some variables, yielding a number of subproblems. We aimed for each single subproblem to be solvable using the CPLEX-7.1 (ILOG CPLEX, see the reference list) integer programming solver within around 6 hours, which permits a size of around 600 variables and 15000 rows on a 1GHz-UltraSparc-III processor. We also adapted the tightness of the approximation dynamically to keep computational effort small, while still guaranteeing a lower bound on the RPLUSC process above the objective value of 185000, which we consider sufficiently high above the known solution for the RDC process with objective 183000.

4. Conclusion

In this paper we studied computer aided design of reaction separation processes for the production of 2,3-dimethylbutene-1 using mathematical optimization methods. First, standard local MINLP solvers were applied to obtain a quick ranking of suitable process candidates. Afterwards, polyhedral relaxations of the feasible region were used to provide global bounds on the objective function value, allowing the comparison of known local optima for different designs. Through that, it can be shown that reactive distillation is most economical for continuous production of DMB-1.

For the second approach, suitable approximations for the different nonlinearities are required. In the present case characteristic nonlinearities are associated with reaction kinetics, phase equilibrium and bilinear terms of the balance equations. Similar nonlinearities will arise in other design applications. Hence, approximating polyhedra for these can be collected and automatically re-used. The strength of the relaxation can be varied as needed by further decomposition of the domains. Here the number of binary variables used to encode the slice in the decomposition grows only linearly for each variable involved, which is important since the difficulty of solving mixed integer programs usually depends more strongly on the number of variables than on the number of constraints. Nevertheless the resulting MILP are computationally challenging. However, the ability to solve mixed integer programming problems has increased tremendously over the last years and is a very active field of research. Current codes can handle problem instances with little structure of around 1000 variables and 20000 constraints, and larger problems if structural knowledge is available. The types of problem generated using polyhedral approximations as we do in this paper have not been studied well; it may well be possible to devise specialized solution techniques

enabling us to solve large instances without as much decomposition as needed in this paper.

References

Brooke, A., D. Kendrick, A. Meeraus, and R. Raman, 1998, GAMS – A user's guide (www.gams.com).

Ciric, A. and D. Gu, 1994, Synthesis of nonequilibrium reactive distillation processes by MINLP optimization. AIChE J., 40, 1479.

Gangadwala, J., A. Kienle, U.-U. Haus, D. Michaels, and R. Weismantel, 2004, Optimal production of 2,3-dimethylbutene-1, to be submitted for publication.

ILOG CPLEX, ILOG, INC., CPLEX, http://www.ilog.com/products/cplex/

Kent, A., M. Lawrenson, and D. Macalpine, 1989, Process for the production of 2,3-dimethylbutene-1 from propene. U.S. Patent 4,835,328.

Krishna, R., 2002, Hardware selection and design aspects for reactive distillation columns, In Sundmacher, K., Kienle A. (Eds.), Reactive distillation - status and future trends, pp. 169 - 189, Wiley-VCH, Weinheim.

Sato, H., H. Tojima, and K. Ikimi, 1999, Studies on nickel-containing Ziegler-type catalysts: V. dimerization of propylene to 2,3-dimethylbutenes. Part III. 1,1,1,3,3,3-Hexafluoro-2-propanol as a new efficient activator, J. Mole. Cat. A: Chem., 144 (2), 285.

Schoenmakers, H. and B. Bessling, 2002, Reactive distillation process development in the chemical process industries, In Sundmacher, K., Kienle A. (Eds.), Reactive distillation - status and future trends, pp. 30 - 48, Wiley-VCH, Weinheim.

Stichlmair, J. and T. Frey, 2001, Mixed-integer nonlinear programming optimization of reactive distillation processes, Ind. Eng. Chem. Res., 40, 5978.

Sundmacher, K., A. Kienle, 2003, Reactive distillation - status and future trends, Wiley-VCH, Weinheim.

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