

MINLP OPTIMIZATION OF CATALYTIC DISTILLATION COLUMNS USING A RATE-BASED MODEL

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This contribution proposes a tool for the computer-aided optimal design of catalytic distillation columns, based on a Mixed Integer Non Linear Programming (MINLP) formulation. This optimization is based on a generic Non Equilibrium Model (NEQ). The objective is to minimize the cost function, finding the optimal parameters of the column: reboiler duty, reflux ratio, feed and reactive tray position, column diameter, etc. In order to achieve global optimization, the solution strategy combines two algorithms: Simulated Annealing (SA) and Successive Quadratic Programming (SQP). Hydrodynamic constraints are included in order to prevent undesirable effects: entrainment flooding, down-flow flooding and weeping-dumping. The catalytic distillation of ETBE (Ethyl tert–Butyl Ether) is discussed as an illustrative example.

KEYWORDS: catalytic distillation, optimal design, MINLP optimization, Non Equilibrium Model

INTRODUCTION

According to the technical importance of multifunctional reactors, many works have been dedicated to catalytic distillation. Research activities have focused principally on three aspects: design, experimental study and simulation. More recently, for economical aspects, the research on catalytic distillation is addressed to the optimal design of this kind of equipment, to contribute directly to decrease the operating and investment costs and to improve the performance of the operation. The objective is to minimize the cost function, finding the optimal operating and design parameters of the catalytic column (Reflux ratio, reboiler duty, feed and catalytic stage location etc.). The optimization is submitted to a set of constraints related to the product specifications. This optimization yields a Mixed Integer Non Linear Programming (MINLP) Problem. The MINLP optimization of the catalytic distillation columns has been already studied by different authors with works based on the equilibrium stage model (Table 1). The main drawback of these models is that the column hardware parameters are not taken into account, so the authors generally have used the concept of tray efficiency. This tray efficiency is difficult to estimate for multi component reactive systems.

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Table 1. Catalytic distillation design

Authors	Ciric and Gu, 1994	Frey and Stichlmair, 2000	Cardoso et al., 2000	Poth et al., 2001
Model	Equilibrium	Equilibrium	Equilibrium	Equilibrium
Reaction	Liq/hom	Liq/het	Liq/hom	Liq/het
Thermodynamics	Ideal	Wilson	Ideal/Wilson	Wilson
Algorithm	GBD	OA/ER/AP	SA/NR	OA/ER/AP
Example	Ethylene Glycol	Methyl Acetate	Methyl Acetate	MTBE
Authors	Jackson and Grossmann, 2001	Poth et al., 2003	Sand et al., 2004	This article
Model	Equilibrium	Equilibrium	Equilibrium	Non-Equilibrium
Reaction	Liq/hom	Liq/het	Liq/het	Liq/het
Thermodynamics	Ideal	Wilson	Wilson	UNIFAC
Algorithm	OA	OA/ER/AP	BB/GRG	SQP/SA
Example	Ethylene Glycol	Methyl Acetate	MTBE	ETBE

OA(/ER/AP): Outer Approximation (/Equality Relaxation/Augmented Penalty); GBD: Generalized Bender's Decomposition; MTBE: Methyl ter Butyl Ether; BB: Branch and Bound; Liq: Liquid phase reaction; NR: Newton–Raphson; hom: homogeneous catalyst; GRG: Generalized Reduced Gradient; het: heterogeneous catalyst

We propose a tool for computer-aided optimal design of catalytic distillation columns, based on a MINLP formulation (Mixed Integer Non Linear Programming). The model introduces two kinds of section: i) Separation sections. These sections are modeled according to the two film theory and it uses mass and heat transfer coefficients to determine the flux at the interface (Integral Non Equilibrium Model). ii) Reactive sections. In this kind of section, the reaction takes place in the liquid phase. The reaction is described using a global kinetic, based on the Langmuir–Hinshelwood–Hougen–Watson. In reactive sections, there is no transfer between liquid and vapor phases. This special configuration (reactive sections and separation sections) has been considered in order to describe our pilot plant column installed at the "Laboratoire de Thermique, Énergétique et Procédés" (LaTEP) in Pau, France. Such configuration has been developed by the French Institute of Petroleum (IFP): the so called CATACOL® technology is used in several industrial columns.

The use of the Integral Non Equilibrium Model presents two major advantages: i) the computation of tray efficiencies is entirely avoided and ii) The geometrical parameters of the column can be optimized. The hydraulic constraints (entrainment flooding, down-flow flooding, weeping-dumping) are also considered.

Due to the complexity of the Non Equilibrium Model, the choice of the solution strategy is a critical point. The suitable solution strategy for the global optimization is a two level proposal that combines two different algorithms: Simulated Annealing and Sequential Quadratic Programming.

In the following section, the model is described. In section 3, we present the formulation of the problem: hypothesis, optimization variables, optimization constraints and objective function. The fourth section is dedicated to the solution strategy. The example (ETBE synthesis), the results and the conclusions are described in sections 5 and 6.

THE MODEL

The first models to describe the catalytic distillation columns were based on the equilibrium stage concept. The main hypotheses for this kind of model are: physical equilibrium on the separation sections and, in most of the works, chemical equilibrium on the reactive sections. With the impossibility to consider the plate geometry, the authors had to introduce the tray efficiency which is difficult to estimated for multicomponent reactive systems and, moreover, makes no physical sense (negative values may occur).

Then many works have addressed the Non Equilibrium Models (Rate Based Models). In these models, mass and heat transfer are described according to the geometrical configuration of the tray (or of the packing if packed column are under consideration).

A pilot plant column is available in the "Laboratoire de Thermique, Energétique et Procédés" (LaTEP) at Pau. As said before, the specific configuration of this column is as follows: separation sections without catalyst; reactive sections with catalyst but without mass transfer (the vapor phase is bypassed). Then we have developed a generic Non Equilibrium Model, adapted to the geometrical configuration of this column.

The separation sections are cross flow sieve trays of a single pass. They are described using an Integral Non Equilibrium Model (NEQ). The hydrodynamic model is based on the two films theory. Thermodynamic equilibrium is achieved at the interface. This model uses multicomponent mass and heat transfer coefficients to determinate the flux at the interface (Krishnamurthy and Taylor, 1985).

According to our pilot plant design, these sections are considered as stirred cell reactors (Figure 1). Inside the reaction stages, one finds the catalyst pellets in direct contact with the liquid flow. One should note that there is no vapor/liquid interface for the reactive sections: the vapor is bypassed in a central tube. When a reactive section is considered, a pseudo-homogeneous reaction term is introduced in the balances of the liquid bulk.

The model considers a total condenser and a partial reboiler with an efficiency equal to unity. We use the classical MESH equations with some modifications for the condenser.

For a system with **nc** components and a catalytic distillation column with **nt** sections, the number of equations and the variables is **5nt + 5nc • nt** (Table 2).

OPTIMIZATION PROBLEM FORMULATION

We minimize an objective function relative to the cost of the process, optimizing the state variables, the operating and the design parameters. In this study, the optimal design of a catalytic distillation column is stated as a MINLP problem since the annualized cost is

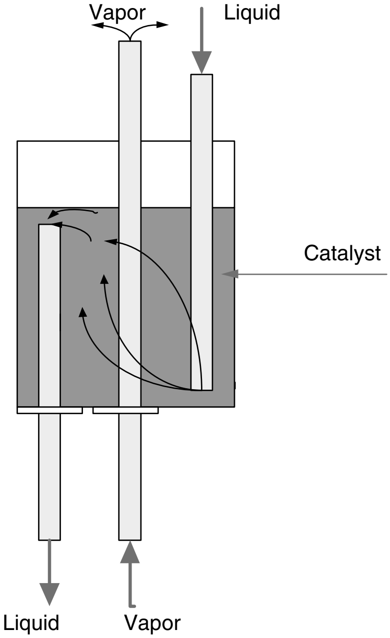

Figure 1. Schematic representation of a reactive stage

minimized according to continuous and discrete variables. The minimization is submitted to a set of non linear constraints.

In the present work, we consider the following hypothesis: the feed rates, the feed compositions and the operating pressure are fixed parameters.

The optimization variables are classified into three groups: the model variables (Table 2), the operating variables and the design variables. The reflux ratio and the reboiler duty are the operating variables. The design variables can be classified into two sub groups: integer variables (number of stages, feed tray location, number of reactive stages, reactive stage location) and continuous variables (weir height, active area, liquid flow path length, column diameter, catalyst loading per stage).

This optimization is submitted to three types of constraints: The model equations (Table 2), the product specification (purity) and the hydrodynamic equations. The hydrodynamic constraints avoid three undesirable effects: entrainment flooding, down flow flooding and weeping-dumping. These constraints ensure the feasibility of the design from a geometrical point of view.

The minimized objective function is the sum of two terms: the Annualized Capital Cost (ACC) and the Annual Operating Costs (AOP). The ACC includes the installed cost

Table 2. Non equilibrium model: equations and variables

Equations of a stage	Variables	Number
Liquid Bulk		
Energy balance	Liquid bulk temperature	nt
Component material balance	Liquid bulk composition	nt • nc
Material balance	Liquid bulk flow rate	nt
Component transfer rate equation	Component transfer rate	nc • nt
Vapor Bulk		
Energy balance	Vapor bulk temperature	nt
Component material balance	Vapor bulk composition	nt • nc
Material balance	Vapor bulk flow rate	nt
Component transfer rate equation	Vapor composition at the interface	nc • nt
Interface		
Equilibrium equation	Liquid composition at the interface	nc • nt
Equality of energy at the interface	Interface temperature	nt
	TOTAL	5nt + 5nc • nt

of the shell, the trays, the reboiler, the condenser and the catalyst, with a 5 year paykback. The AOP involves the consumption of raw material, steam and cooling utility. The value of the different products is also included in the AOP (Ciric and Gu, 1994).

$$FOB_J = \min\left\{ \sum_{i=1}^{nc} C_i \sum_{k=1}^{nt} F_{ik} + C_H Q_B + C_W Q_C + A_F(C_{CS} + C_{CI} + C_r + C_C) \right\}$$

where (nc) is the number of components, (nt) the number of trays (separation and reaction), (C_i) the raw material cost or the product value [$\$ \cdot mol^{-1}$], ($F_{ik}$) the partial flow rate of a component k in feed i [$mol \cdot yr^{-1}$], (C_H) the heating cost [$\$ \cdot W^{-1} \cdot yr^{-1}$], ($C_W$) the cooling cost [$\$ \cdot W^{-1} \cdot yr^{-1}$], ($A_F$) the annualizing factor [yr^{-1}], (Q_B) the reboiler duty [W], (Q_C) the condenser duty [W], (C_{CS}) the installed cost of the shell [$], ($C_{CI}$) the installed cost of the trays and the reactive sections [$], ($C_r$) the installed cost of the reboiler [$] and ($C_C$) the installed cost of the condenser [$].

The formulated problem is a Mixed Integer Non Linear Programming (MINLP) problem. For a system with **nc** components, and a column with **nt** sections (reactive and separation), there are a total of **14 + 9nt + 4nc + 5nt • nc** variables to be optimized, including **3nt + 1** integer variables. The problem includes **11 + 5nt + 4nc + 5nt • nc** non linear equality constraints and **3** nonlinear inequality constraints.

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SOLUTION STRATEGY

In order to solve this MINLP non convex optimization problem, we propose a solution strategy that combines Simulated Annealing (SA) and Successive Quadratic Programming (SQP). A Non Linear Programming sub problem is formulated and solved using SQP, a deterministic algorithm. Most of the continuous variables (model variables, operating parameters and catalyst loading per stage) are considered at this level. Integer and remaining continuous variables are optimized at the level of the MINLP Master Problem which is solved using SA (Figure 2).

The Simulated Annealing is a well known stochastic and direct method, for global optimization. With our solution strategy, design variables (except: catalyst loading per stage) are generated randomly, allowing wrong way movements to increase the probability of convergence toward the global optimum or, at least, to a near optimum solution. At this MINLP level, the objective cost function is augmented with a penalization term, in order to satisfy the hydraulic constraints.

The set of variables proposed by the Simulated Annealing are sent to the NLP level. The cost minimization is submitted to the model equations and the product specification. This sub problem is solved using a particular SQP algorithm (QPKWIK), based upon the dual algorithm of Goldfard and Idnani and developed by Schimd, Lorenz and Biegler in Carnegie Mellon University (Schmid and Biegler, 1994). We have experienced that the initialization and the bounding of the variables are critical points of the successful

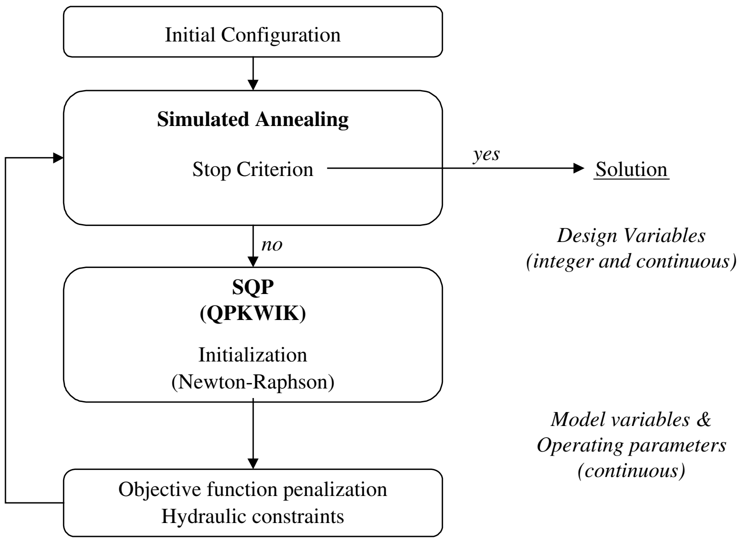

Figure 2. Solution strategy

optimization. For this reason, at the initialization step, the catalytic distillation model is solved using Newton-Raphson method.

This two stage solution strategy results in a trade off between a deterministic and a stochastic method. This procedure can be justified as follows: With local deterministic MINLP optimization techniques, such as Branch and Bound, Outer Approximation or Generalized Bender's Decomposition, depending on the initial point, the probability to reach the global optimum is quite weak if the problem is non convex or highly non linear. On the other hand, the solution of large-scale process optimization problems, using Simulated Annealing (or any other stochastic method) is quite difficult and computationally expensive. The choice of the QPKWIK algorithm is based on its capability to solve problems with large number of equations, but relatively few degree of freedom.

ILLUSTRATIVE EXAMPLE AND RESULTS

The illustrative example is the production of ETBE by catalytic distillation, as a main product. The importance of this reaction resides in the growing worldwide consumption of this product: in the EU, from 2003 to 2004, the ETBE production has been increased by 9.48%. This reaction has been treated by several authors with promising results (Sneeby et al., 1997; Al-Arfaj and Luyben, 2002; Young and Lee, 2003). The reaction to produce ETBE from Ethanol (EtOH) and Isobutene (IB), is an acid catalyzed (Amberlyst 15®) reversible etherification, moderately exothermic that takes place in the liquid phase. The kinetic used in this work corresponds to an expression based on the Langmuir–Hinsherwood–Hougen–Watson (LHHW) (Al-Arfaj and Luyben, 2002).

The liquid phase is strongly non ideal: activity coefficients are evaluated using the UNIFAC model.

The objective of this example is to improve (optimize) an initial feasible configuration. The specification of the product is assumed to be 80 mol% minimum of ETBE. The cost of raw material are: EtOH 15$\$\cdot kmol^{-1}$; Butenes (iso + normal) 8.25$\$\cdot kmol^{-1}$; Catalyst 7.7$\$ \cdot kg^{-1}$ (Al-Arfaj and Luyben, 2002). The value of product is 25.3$\$ \cdot kmol^{-1}$.

The following parameters are fixed: operating pressure (950000 Pa), hole pitch (0.008 m), tray spacing (0.15 m) and the number of feeds (2). The stages (reaction or separation) are numbered from the top to the bottom, not including the condenser nor the reboiler.

Table 3. Column feed

Feed	Temp K	Flow rates $mol \cdot s^{-1}$	X_{EtOH} molar	X_{IB} molar	X_{ETBE} molar	$X_{n\text{-}B}$ molar
1	323	0.02853	1.0	0.0	0.0	0.0
2	357	0.091135	0.0	0.3	0.0	0.7

The initial and de final configurations, fulfilling the hydraulic and purity constraints, are described in Table 4. The final solution has 400 grams of catalyst on each reactive section. This is the upper bound of the variable with the mechanical configuration of the column. The saturation of these variables indicates that the reactive section location is adapted to the reaction conditions: a bad location makes the optimizer moves the catalyst load toward the lower bound of the variable, which is fixed at 100 grams for this example.

The total annualized cost for the initial configuration is 10757$ $\cdot$ yr^{-1}. For the optimal configuration, the total annualized cost is equal to 6854$ $\cdot$ yr^{-1}. The raw material cost and the product value are much greater than the construction and the installation cost

Table 4. Initial and final configuration

Variable	Initial configuration	Final configuration
Column diameter (m)	8×10^{-2}	8.2×10^{-2}
Reflux ratio	5.05	5.34
Reboiler duty (W)	7991.65	7197.45
Weir height (m)	2×10^{-2}	2.1×10^{-2}
Weir length (m)	6.4×10^{-2}	6.62×10^{-2}
Active area (m^2)	3.59×10^{-3}	3.85×10^{-3}
Flow path length (m)	0.04800	0.05303
Hole area (m)	4.58×10^{-4}	4.91×10^{-4}
First feed location	4	7
Second feed location	25	23
Number of reactive sections	3	8
Reactive section location	11,13,15	7,9,12,14,16,17,20,22
Number of trays	30	39

Table 5. Initial and final annualized cost

Annualized cost ($ $\cdot$ an^{-1})	Initial configuration	Final configuration
Cost of raw material	20 326	20 326
Value of product	−21 040	−24 831
Cost of catalyst	2	5
Operating cost of condenser	1 174	1 058
Operating cost of reboiler	204	188
Installed cost of equipment	10 091	10 108

of the column. However the geometrical characteristics of the trays have a direct incidence on mass and heat transfer, that in turn, have a strong influence on the production and, consequently, on the cost function (Table 5).

CONCLUSION

The optimal design of a catalytic distillation column, based on a non equilibrium (NEQ) model was presented. To solve this MINLP problem, we propose a strategy that combines Simulated Annealing (SA) and Sequential Quadratic Programming (SQP). Considering the ETBE illustrative example, the results indicate that the propose algorithm is capable to minimize the objective function submitted to a set of constraints (product specification and hydraulics): a new column configuration is proposed with a significant cost reduction. The use of Murphree tray efficiencies was avoided. The optimized tray configuration satisfies the hydraulic constraints in order to guarantee the correct design of the column.

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