

## A "MINLP" Formulation for Optimal Design of a Catalytic Distillation Column Based on a Generic Non Equilibrium Model

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### Abstract

This contribution proposes a Mixed Integer Non Linear Programming (MINLP) formulation for optimal design of a catalytic distillation column based on a generic non-equilibrium model (NEQ). The solution strategy for the global optimization combines Simulated Annealing (SA) and Sequential Quadratic Programming (SQP) in order to minimize the objective function. The solution of this MINLP problem yields the optimal values for the temperature, composition and flow rate profiles, tray geometry, column diameter, reflux ratio, reboiler duty, feed tray location, number of trays and catalytic stage location. Hydraulic constraints (entrainment flooding, down-flow flooding, weeping-dumpling) are also considered. For the example, the production of ETBE (Ethyl tert-butyl ether) is presented here.

**Keywords:** Catalytic Distillation, Non equilibrium model, MINLP Optimization.

### 1. Introduction

Reactive distillation (RD) is a multifunctional reactor concept which combines a distillative separation with a chemical reaction. More specifically, the catalytic distillation (CD) is a process where chemical reaction occurs over a solid catalyst and the ensuing mixture of reactants and products is separated by fractional distillation. There are three possible advantages of catalytic distillation over the conventional process (reactor + distillation column): Higher conversion, improved selectivity and heat integration. These contribute directly to lessening the initial investment and to reducing operating cost. For all of these reasons, the use of these equipments has grown in recent years.

The MINLP optimization of a CD column has been already studied by different authors with steady-state models in which the vapour and liquid are assumed to be in equilibrium (Ciric and Gu, 1994 ; Frey and Stichlmair, 2000 ; Cardoso et al, 2000 ; Poth et al, 2001 ; Jackson and Grossmann, 2001 ; Sand et al, 2004). In these works, the

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authors use the MESH equations. The main drawback with these equations is that the column hardware parameters (the diameter and the tray configuration) are not taken into account directly, so the authors generally use the concept of tray efficiency which is very difficult to estimate for multi-component, reactive systems.

The Laboratoire de Thermique, Energétique et Procédés (LaTEP), in collaboration with The Laboratoire de Genie Chimique (LGC), has been working since 1999 to propose a software tool (Codicat - NEQ) for the optimal design of the catalytic distillation, based on a MINLP formulation and on a generic non-equilibrium model (NEQ). According to our pilot plant, provided by the French Institute of Petroleum, the model involves two kinds of sections: i) separation sections, without reaction, which use mass and heat transfer coefficients to determine the flux at the liquid/vapour interface, ii) reactive sections, where the reaction takes place; one finds the catalyst pellet in direct contact with the liquid flow, but not with the vapour flow. This configuration (separation / reaction section) allows to use the mass and heat transfer coefficients for non- reactive systems. The use of this NEQ model for the column optimization presents two main advantages: i) the computation of tray efficiencies are entirely avoided; ii) the geometrical parameters of the column's hardware can be optimized. The hydraulic constraints (entrainment flooding, down-flow flooding, weeping-dumping) are also considered. Of course the main drawback is that the NEQ model is more complex.

The solution strategy suitable for the global optimization is based on a proposal that combines Simulated Annealing and Sequential Quadratic Programming in two levels. The role of the simulated annealing is to generate a set of random variables and to allow simultaneously wrong-way movements, proving convergence to the global optimum. For fixed values of certain optimization variables, the resulting Non Linear Programming (NLP) sub- problem is solved using an SQP algorithm.

For its increasing technical importance, the synthesis of ETBE is investigated as example in this study.

## 2. The Column Model

### 2.1 Separation stages

The separation sections (separation stages) are cross flow sieve trays, of a single pass. The condenser is considered to be total and the reboiler is considered an equilibrium stage (with classical MESH equations). The separation sections are described using an integral non equilibrium model (NEQ). This model is based on the two films theory and uses mass and heat transfer coefficients to determine the flux at the interface. The equations used to model the behaviour of these stages are the conservation equations, the rate equations and the interface models. For more details, please refer to the works of Krishnamurthy and Taylor, 1985. For a CD column with NT number of trays and NC number of components, the total number of equations and variables is:  $5.NT+5.NC.NT$ .

The transfer rate equations, for liquid and vapour are stated as follows:

$$(N_j) = c_{ij}^V \left[ k_j^V \right] a_j \left( x_j^V - x_j^{VI} \right) + N_{ij}^V \quad (1)$$

$$(N_j) = c_{ij}^L \left[ k_j^L \right] a_j \left( x_j^{LI} - x_j^L \right) + N_{ij}^L \quad (2)$$

## 2.2 Reactive sections

Inside of the reaction sections (reactive stages), one finds the catalyst pellet in direct contact with the liquid flow, but not with the vapour flow. These reactive sections are considered to be stirred cell reactors.

## 3. Formulation of the Optimization Problem

### 3.1 Hypothesis

In the present work, the feed rates, the feed compositions and the operational pressure are fixed parameters.

### 3.2 Optimization variables

The optimization variables can be classified into two groups, integers and continuous variables. The first ones are feed tray location, catalyst location and number of trays. The second one, can be classified also into three sub-groups: i) operational variables as reflux ratio and reboiler duty, ii) model variables as liquid bulk temperature, liquid bulk compositions, liquid bulk flow rate, component transfer rates, vapour bulk temperature, vapour bulk compositions, vapour bulk flow rate, vapour compositions at the interface, liquid compositions at the interface and interface temperature, iii) design variables as weir height, active area, column diameter, liquid flow path length, weir length and catalyst load per stage.

### 3.3 Optimization Constraints

The optimization is submitted to three sets of constraints: The model equations, the product specification and the tray hydrodynamic equations. All the variables are bounded with physical criteria. The restrictions that the hydrodynamic equations impose on the geometrical design of the plate and on the diameter, avoid three undesirable effects on the tower: Entrainment flooding, dow-flow flooding, weeping-dumping.

### 3.4 Objective Function

The objective is to minimize the total annualized investment and operating cost. As an approach of optimization, the following function is used (Cardoso et al, 2000).

$$FOB_j = \min \left\{ \sum_{i=1}^{NC} C_i \sum_{k=1}^{NT} F_{ik} + C_H Q_B + C_W Q_C + A_F (C_{CS} + C_{CI} + C_r + C_C) \right\} \quad (3)$$

Where: NC number of components, NT number of stages,  $C_i$  cost of the raw material or value of the product ( $\$.mol^{-1}$ ),  $F_{ik}$  feed rate of raw material or product ( $mol.yr^{-1}$ ),  $C_H$  cost of steam ( $\$.W^{-1}.yr^{-1}$ ),  $C_W$  cost of cooling water ( $\$.W^{-1}.yr^{-1}$ ),  $A_F$  Annualing factor ( $yr^{-1}$ ),  $Q_B$  reboiler duty (W),  $Q_C$  condenser duty (W),  $C_{CS}$  installed cost of column shell (\$),  $C_{CI}$  installed cost of trays (\$),  $C_r$  installed cost of reboiler (\$),  $C_C$  installed cost of condenser (\$).

This problem is a Mixed Integer Non linear Programming (MINLP). The total number of variables to optimize is  $14+4.NC+10.NT+5.NC.NT$ , where  $4.NT$  are integer variables and the total number of constraints is  $12+NC+5.NT+5.NC.NT$ .

## 4. Solution Strategy

The solution strategy suitable for the global optimization is based on a proposal that combines Simulated Annealing and Sequential Quadratic programming (NLP problem) in two different levels. The role of Simulated Annealing is to propose a set of random integer variables, and design variables (except catalyst load per stage), allowing wrong way movements to increase the probability of convergence toward the global optimum or at least, the location of near-optimum solution. In order to minimise the objective function, the NLP sub-problem optimise the model, the operational and the catalyst load per stage variables. This minimisation is submitted to the model equations and the product specification. This sub-problem is solved using a SQP algorithm (QPKWIK), based upon the dual algorithm of Goldfarb and Idnani, developed by Schmid, Lorenz and Biegler in Carnegie Mellon University (Schmid and Biegler, 1994). The restrictions imposed by the hydraulic constraints penalize the cost function at the level of the Simulated Annealing.

To make the algorithm more reliable, an initialization with Newton-Raphson method has been carried out. The latter strategy was adopted after considering several propositions for the following reason: the solution of large-scale problems with the only use of a stochastic method is quite impossible, because it is computationally expensive. The Branch and Bounds method (BB), the Outer Approximation/Equality-Relaxation (OA/ER) or the Generalized Benders Decomposition (GBD) may be trapped in a local minimum since the optimization problems is a highly non linear, non-convex problems. Thus, the proposed two stage solution strategy seems to be the most suitable. The Sequential Quadratic Programming is a well adapted algorithm to solve the NLP problem in question ; it has been especially useful for a wide variety of process with many variables and constraints but with only a low degree of freedom. On the other hand, the Simulated Annealing method is a well established technique for the optimization of combinatorial problems that assumes numerous discrete configurations. Consequently the strategy adopted for this study is based on the combination of these two algorithms.

## 5. Example and Results

To illustrate the optimization, we analyze the ETBE production by catalytic distillation. The ETBE is an important gasoline oxygenates because it is classified as semi renewable when the ethanol (EtOH) reactant is derived from biomass. This reaction has been treated by several researchers with encouraging results (Sneeby et al, 1997 ; Al-Arfaj and Luyben, 2002 ; Young and Lee, 2003). The formation of ETBE from ethanol and isobutene (IB) is an acid catalyzed (Amberlys 15®), reversible, moderately exothermic reaction. The reaction Kinetics is based on the Langmuir-Hinshelwood-Hougen-Watson model. (for more details, see Al-Arfaj and Luyben, 2002.) The modified UNIFAC (Dortmund) model for the prediction of the activity is used because the ETBE reaction system is highly non-ideal.

The goal of this example is to optimize an initial feasible configuration. The specification for the bottom product is assumed to be 80 mol % minimum of ETBE. The

cost of raw material are: EtOH 15 \$.kmol<sup>-1</sup>; Butenes (iso + normal) 8.25 \$.kmol<sup>-1</sup>; Catalyst 7.7 \$.kg<sup>-1</sup> (Al-Arfaj and Luyben, 2002). The value of product is 25.3 \$.kmol<sup>-1</sup>. The following parameters are fixed: operational pressure (950000 Pa), hole pitch (0.008 m), tray spacing (0.15 m) and the number of feeds (see table 1). The stages (reaction or separations) are numbered from top to bottom, not including the condenser nor the reboiler.

Table 1. Column feed

Feed	Initial Tray	Optimal Tray	Temp K	Flow rate mol.s <sup>-1</sup>	X <sub>EtOH</sub> molar	X <sub>IB</sub> molar	X <sub>ETBE</sub> Molar	X <sub>n-B</sub> molar
1	4	7	323	0.02853	1.0	0.0	0.0	0.0
2	25	23	357	0.091135	0.0	0.3	0.0	0.7

The initial and the optimal configurations, fulfilling the hydraulic and purity constraints, are described in the table 2.

Table 2. Initial and final configuration.

Variable	initial Configuration	final Configuration
Column diameter (m)	8 x 10 <sup>-2</sup>	8.2 x 10 <sup>-2</sup>
Reflux ratio	5.05	5.34
Reboiler duty (W)	7991.65	7197.45
Weir height (m)	2 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>
Weir length (m)	6.4 x 10 <sup>-2</sup>	6.62 x 10 <sup>-2</sup>
Active area (m <sup>2</sup> )	3.59 x 10 <sup>-3</sup>	3.85 x 10 <sup>-3</sup>
Distance traveled by liquid on a tray (m)	0.04800	0.05303
Hole area (m)	4.58 x 10 <sup>-4</sup>	4.91 x 10 <sup>-4</sup>
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

The final solution has 400 grams of catalyst on each reactive section. This is the maximum quantity possible with the mechanical configuration of the column. The saturation of these variables indicates that the position of the reactive section is adapted to the reaction condition, because a bad location makes the optimizer moves the catalyst load toward the minimum allowed value which is fixed at 100 grams for this example. The total annualized cost for the initial configuration is 10757 \$.yr<sup>-1</sup>. and for the optimal configuration is 6854 \$.yr<sup>-1</sup>. The cost of raw material and the value of the product are much greater than the construction and the installation cost of the column. However the geometrical characteristics of the tray 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 (see table 3).

Table 3. Initial and final annualized cost

Annualized cost (\$/yr <sup>-1</sup> )	Initial configuration	Final configuration
Cost of raw material	20 326	20 326
Value of product	-21 040	-24 831
Cost of catalyst	2	5
Operational cost of condenser	1 174	1 058
Operational cost of reboiler	204	188
Installed cost of equipment	10 091	10 108

## 6. Conclusion

A mixed integer non linear programming problem was presented for the optimal design of a catalytic distillation column with a non equilibrium model. To solve this MINLP problem, a new solution strategy was investigated and the results indicate that the proposed optimization algorithm is capable to optimize an initial configuration submitted to a set of constraints. The use of Murphree tray efficiencies was avoided and the solution satisfies the hydraulics constraints in order to guarantee the correct design of the column.

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