# Exergy analysis and optimization of reactive distillation column in acetic acid production process

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## ABSTRACT

Exergy analysis method is applied to evaluate the performance of reactive distillation (RD) column in the acetic acid production process, at which acetic acid is produced via reaction between carbon monoxide and methanol with a soluble catalyst system consisting of rhodium complex (catalyst) and methyl iodide-hydrogen iodide (promoter). In this column, desired purity of the product is obtained through reaction between methanol and hydrogen iodide. The effects of different operational parameters on the separation and the exergy efficiencies of this RD column are evaluated by sensitivity analysis, finally, the response surface methodology (RSM) method is applied for modeling and optimization of the exergy loss. The adequacy of the developed model for exergy losses in the reactive distillation column is evaluated using analysis of variances (ANOVA). The result of ANOVA study shows that the most effective operating parameters are feed stream temperature, boilup ratio, and reflux ratio. As the result of this optimization the exergy losses and energy consumption for the reactive distillation column reduced by 28% and 12% respectively. This study shows that RSM method besides the exergy concept could be an appropriate tool for optimization of complex and energy intensive reactive distillation systems.

## 1. Introduction

Exergy analysis is a novel method for design and optimization of chemical processes that is widely applied by researchers in last three decades. The concept of exergy is based on the first and second laws of thermodynamics, which considers the quality of energy as a tool to specify the sources of inefficiency and potential for improvement in chemical processes [1,2]. Distillation as one of the most energy intensive separation techniques is widely used in chemical production processes so it is very necessary to design energy-efficient distillation systems and to specify operating conditions that minimize the consumption of energy in distillation systems [3]. Many studies have been undertaken to conduct exergy analysis of distillation columns [4–14]. The results of these studies reveal that exergy analysis technique is an applicable tool for improving the performance of distillation columns. Bandyopadhyay [15] presented a general methodology based on exergy loss analysis to evaluate the performance of a distillation column for the different thermal condition of the feed. Effect of operating parameters on the thermodynamic efficiency of a distillation column was evaluated by Bandyopadhyay, these parameters include feed composition, thermal condition of the feed, the relative volatility of its components and sharpness of separation. Sun et al. [13] applied exergy analysis method to improve energy efficiency of a methanol distillation scheme,

the results show that the energy consumption of the five-column distillation scheme can be reduced by 15.23% and that the total exergy loss can be decreased 21.5% in comparison to the popular four-column methanol distillation scheme. Khoa et al. [12] proposed a new exergy graphical method for optimal design of distillation column with minimum exergy loss, in this new method the effect of design and operating parameters of a distillation column on the exergy loss is graphically visualized by three-dimensional exergy analysis curves. In the conventional distillation columns the main reasons for exergy dissipation include: exergy loss owing to cooling, heating, mixing in the vapour and liquid phases, condensation, evaporation and pressure drop across the column [15,16]. However, the situation for reactive distillation columns is more complex; due to the chemical reactions take place in these columns, the exergy loss for the reactive distillation columns is much more than the exergy loss for the conventional distillation columns. Reactive distillation is a state of the art technology that combines the distillation and the chemical reaction in one single operating step [17]. The combination of both reaction and separation tasks in a unique unit operation leads to many advantages, including improved conversion and selectivity, reduced catalyst requirement and by-product formation, avoidance of azeotropes and heat integration benefits. However, due to the complexities of reactive distillation columns, they are not suitable for many reaction systems. The combination

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**Nomenclatures**

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| $Ex$ | Exergy [kJ/h] |
| $Ex^{Ph}$ | Physical exergy [kJ/h] |
| $Ex^{Ch}$ | Chemical exergy [kJ/h] |
| $T$ | Temperature [K] |
| $T_0$ | Ambient temperature [K] |
| $P$ | Pressure [kPa] |
| $P_0$ | Ambient pressure [kPa] |
| $H$ | Enthalpy [kJ/kmol] |
| $H_0$ | Enthalpy at ambient conditions [kJ/kmol] |
| $S$ | Entropy [kJ/kmol K] |
| $S_0$ | Entropy at ambient conditions [kJ/kmol K] |
| $x_i$ | Liquid phase mole fraction [−] |
| $y_i$ | Vapor phase mole fraction [−] |
| $L$ | Liquid phase molar flow rate [kmol/h] |
| $V$ | Vapor phase molar flow rate [kmol/h] |
| $\varepsilon_i^{0l}$ | Standard chemical exergy in liquid phase [kJ/kmol] |
| $\varepsilon_i^{0v}$ | Standard chemical exergy in vapor phase [kJ/kmol] |
| $\mu_i$ | Chemical potential of each species in the stream [kJ/kmol] |
| $\Delta_{Mix}E$ | Chemical term of chemical exergy [kJ/h] |
| $E_{Mix}$ | Mixture term of chemical exergy [kJ/h] |
| $Ex^Q$ | Exergy of heat [kJ/h] |
| $Q$ | Heat [kJ/h] |
| $r$ | Reaction rate [kmol/h] |
| $k$ | Rate constant [m$^6$/kmol h] |
| $T_r$ | Temperature of heat source [K] |
| $\dot{m}$ | Molar flow [kmol/h] |
| $\dot{W}$ | Shaft work rate [kJ/h] |
| $\dot{Irr}$ | Exergy loss rate [kJ/h] |
| $\psi$ | Rational exergy efficiency [−] |
| $\Delta\dot{Ex}_{in}$ | Exergy transfers making up the input [kJ/h] |
| $\Delta\dot{Ex}_{out}$ | Exergy transfers making up the output [kJ/h] |

of reactions and distillations is possible only if the operational ranges of both unit operations overlap in a sufficient broad region. In the other words, required operational pressure and temperature for distillation must be sufficient for a reasonable conversion of reactions. In some studies the exergy analysis method is applied to evaluate the performance of reactive distillation columns [16,18,19]. Rivero and Garcia [19] performed exergy analysis of a reactive distillation MTBE unit. The results indicate that the main exergy losses of the MTBE plant occur in the reactive distillation unit. A parametric study was conducted in order to find the optimal operating conditions. Kusumaningtyas et al. [16] applied the graphical exergy analysis method to investigate the performance of reactive distillation column for biodiesel production. Their simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system.

There are numerous studies on the modeling and simulation of the reactive distillation columns [20–24]. Applying the equilibrium stage model and efficiency approaches for modeling and simulation of complex systems such as reactive distillations columns bring some uncertainty. In order to obtain reliable results, it is required that a rigorous model such as rate based model for simulation of reactive distillation columns. In the equilibrium stage approach, it is assumed that vapor and liquid phases to be in thermodynamic equilibrium in a stage. While, in the rate based approach the mechanical and geometrical properties of the column (such as height and diameter of the column, type and size of the packings or trays and so on) are used to evaluate the actual rates of multicomponent mass transport, heat transport and chemical reactions directly in the equations governing the stage phenomena [25]. Taylor and Krishna [17] reviewed various aspects of reactive distillation modeling and emphasized on the validation of the simulation results through comparison with the experimental or field data. In recent studies on RD modeling, RADFRAC module in Aspen Plus process simulator is widely used to simulate the reactive simulation columns. It seems that by selecting an appropriate

thermodynamic model, Aspen Plus is a good simulator for reactive distillation columns.

Response surface methodology (RSM) is a well-known statistical optimization method that is widely used for process design and optimization. RSM is a set of mathematical and statistical techniques that are applied for modeling and analyzing of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [26]. As far as known, no study has been done on the application of RSM method in exergy loss optimization.

In this study, we apply the exergy analysis method to evaluate the performance of the reactive distillation column in the acetic acid production plant. Aspen Plus is applied to simulate the RD column according to data from an industrial column operating in one of the Iranian petrochemical companies. The effects of different operational parameters on the exergy losses are investigated through sensitivity analysis. Finally, RSM method is applied to optimize operating parameters. In this optimization framework, the aim is minimizing exergy loss as the objective function, subject to engineering and operational constraints.

## 2. Exergy analysis

### 2.1. Basic concepts of exergy

Exergy is defined as the amount of useful work obtainable when the system is brought to a state of thermodynamic equilibrium with its surrounding by means of reversible processes. In other words, the maximum amount of work that can be obtained from a system by moving it from a particular thermodynamic state to a state of equilibrium with its surrounding (zero exergy state) is defined as exergy [1].

In its general form, Exergy (*Ex*) of a stream of mater is classified in Physical, Chemical, Kinetic and Potential forms however, the Potential and Kinetic forms of exergy can be neglected in comparison to other

**Table 1**
Standard chemical exergy of materials.

| Component | Standard chemical exergy in vapor phase $\varepsilon_i^{0v}$, kJ/kmol | Deviation from values reported in Kotas [2]. (%) | Standard chemical exergy in liquid phase $\varepsilon_i^{0l}$, kJ/kmol | Deviation from values reported in Kotas [2]. (%) |
|---|---|---|---|---|
| Methanol | 727,538 | – | 723,918 | 0.5 |
| Methyl iodide | 789,865 | – | 787,503 | – |
| Methyl acetate | 1,612,547 | – | 1,609,329 | – |
| Acetic acid | 914,258 | 1 | 905,183 | 0.8 |
| water | 11,079 | 5 | 3251 | 4 |
| Hydrogen iodide | 151,116 | – | 150,909 | – |
| Propionic acid | 1,596,267 | – | 1,593,081 | 2 |