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Determination of Operating Parameters of The Reactive Distillation Column for Methyl Acetate Production and Dynamic Simulation of Process

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Metil Asetat Üretiminin Yapıldığı Tepkimeli Damıtma Kolonunun İşletim Parametrelerinin Belirlenmesi ve Prosesin Dinamik Simülasyonu

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Abstract

This study focuses on the simulation of a reactive distillation column used for the production of methyl acetate via the reaction between methanol and acetic acid. Using Chemcad software, a model for the methyl acetate production process was designed, incorporating a reactive distillation column. Based on the design, simulations were conducted, analyzing both steady-state and dynamic conditions. The study identified optimal operating conditions by considering parameters affecting product yield, such as feed rate, recycle flow rate, and feed temperature. Relationships between variables were evaluated, and significant insights were derived regarding the reactive distillation process. Additionally, the process was designed to consider environmental factors while supporting the profitability goals of businesses. Methyl acetate, a key organic raw material, is widely used across industries, including pharmaceuticals, paints, varnishes, plastics, essences, adhesives, artificial leather, coatings, cosmetics, solvents, resins, and certain oils.

Keywords: *Reactive distillation; Methyl acetate; Simulation; Process design.*

Öz

Bu çalışma, metanol ve asetik asidin tepkimeye girerek metil asetat üretimini sağlayan tepkimeli damıtma kolonunun simülasyonunu ele almaktadır. Chemcad yazılımı kullanılarak, tepkimeli damıtma kolonuyla metil asetat üretim sürecinin modeli tasarlanmıştır. Bu tasarıma dayalı olarak gerçekleştirilen simülasyonlar sonucunda, hem kararlı hem de dinamik durum analizleri yapılmıştır. Çalışmada, besleme oranı, geri döngü akışkan miktarı ve besleme sıcaklığı gibi ürün verimini etkileyen parametreler göz önünde bulundurularak en uygun işletme koşulları belirlenmiştir. Simülasyon sonuçları ile değişkenler arasındaki ilişkiler değerlendirilmiş ve tepkimeli damıtma süreci üzerine önemli çıkarımlar yapılmıştır. Böylece, rekabetçi, işlevsel ve yüksek verimliliğe sahip bir süreç tasarımı oluşturulması hedeflenmiştir. Çevresel faktörlerin de dikkate alındığı bu üretim sürecinin, aynı zamanda işletmelerin karlılık hedeflerini desteklemesi amaçlanmaktadır. Metil asetat, endüstride geniş kullanım alanlarına sahip önemli bir organik hammaddedir. Başlıca kullanım alanları arasında ilaç, boya, vernik, plastik, esans, yapıştırıcı, yapay deri, kaplama malzemeleri, kozmetik, çıkarıcılar, reçineler ve bazı yağların üretimi ya da çözücü olarak kullanımı sayılabilir.

Anahtar Kelimeler: *Tepkimeli damıtma; Metil asetat; Simülasyon; Proses tasarım.*

1. Introduction

The rapid growth of the global population, coupled with the expansion of the chemical industry, has made the efficient use of limited and non-renewable resources more critical than ever. Technological advancements in the chemical field have brought significant innovations. Research on reactive distillation has great importance from environmental, economic, and technical perspectives. Today, the chemical industry is responsible for approximately one-third of the total energy consumption and carbon dioxide emissions in the industrial sector. Distillation accounts for over 40% of the energy consumed by the chemical industry, highlighting the need for improvements in this area. Modern chemical plants increasingly require advanced distillation technologies—such as reactive distillation, divided-wall columns, thermal couplings, cyclic distillation, heat pump-assisted distillation, and heat-integrated distillation columns—that can significantly reduce energy consumption and carbon footprints. There are various challenges and opportunities in rethinking energy usage for a more sustainable chemical industry. The methods used in experimental studies must be presented in a detailed and explanatory manner. These methods should

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be defined in a way that allows for reproduction by other researchers. For theoretical studies, previously derived formulas should be referenced, with each quantity explained; otherwise, the necessary derivations should be outlined (Kiss and Smith, 2020).

Within these studies, efficient use of time, energy, and other resources should be ensured, production processes should be approached with environmental sensitivity, and production costs should be minimized. Businesses that aim to remain competitive in the international arena without compromising environmental awareness can only achieve their goals through effective and controllable production process designs. To ensure the achievement of increasing environmental sensitivities, sustainability, and reduced resource consumption—essentially, the implementation of green production principles—industrial process designs must be functional and efficient, which is both a necessity and a responsibility to future generations. In this context, design and optimization studies aimed at maximizing efficiency while minimizing resource use during production are being carried out.

Ester compounds are widely used in the chemical industry as raw materials in various processes. Ethyl acetate and methyl acetate are among the most important and widely used esters of industrial significance. Esterification reactions are equilibrium-limited processes, and post-reaction, they typically require a series of separation steps. Reactive distillation solves this issue by combining chemical reactions and separation processes within a single unit, shifting the equilibrium towards product formation and increasing conversion and selectivity (Bayram and Günay, 2021).

Moraru et al. (2021) studied the production of methyl methacrylate, a key chemical used as a raw material for methacrylates and poly-methyl methacrylate. They conducted process simulations using Aspen Plus and Aspen Plus Dynamics to design and control the production process. The production flow diagram consisted of a fixed-bed reactor followed by three distillation columns, combined with a filtration unit. Their study demonstrated the technical feasibility, energy efficiency, and cost-effectiveness of the proposed process, requiring only 2.05 MJ/kg of methyl methacrylate and achieving a 99.7% carbon efficiency.

Similarly, Andres et al. (2020) designed a reactive distillation process for isobutyl acetate synthesis using a conceptual design methodology based on static and reactive residue curve analysis. The procedure comprised esterifying isobutanol with acetic acid in a heterogeneous catalytic system using Amberlyst 15 as a catalyst. Validated phase equilibrium and kinetic models served as the foundation for their design process. On the basis of predicted products, equilibrium lines, and residue curves, static analysis assisted in locating the reaction zone inside the column. In order to maximize conversion and produce high-purity isobutyl acetate, they determined the critical variables. By optimizing these variables, they were able to minimize energy and capital expenditures while maximizing economic potential. Their optimization reduced the production cost of isobutyl acetate to 0.98 USD/kg. While they concluded that pure isobutyl acetate could not be obtained as a top product from the reactive distillation column, they suggested that it could be obtained as a sufficiently pure bottom product to meet urethane-grade specifications.

Muthia et al. (2019) highlighted that, while reactive distillation offers significant benefits such as cost reduction and energy savings, research and development (R&D) processes often require extensive studies and rigorous simulations, making these tasks complex. To mitigate this complexity and reduce the time required, they proposed a novel graphical method to quickly gain insight into the applicability of reactive distillation for reversible quaternary systems. Using this graphical method, rapid results were obtained regarding the preliminary economic ranking of reactive distillation processes and optimum feed conditions with reduced energy requirements (i.e., lower reflux ratio). They also noted that the boiling point order of the components has significant effects on reactive distillation integration systems, and that the graphical method was highly useful for identifying regions where optimal feed conditions are achieved. For all groups they formed, they noted that shorter distances between the two feed inputs and the introduction of heavier reactants below lighter ones always resulted in benefits.

With an emphasis on tray columns, Bangga et al. (2018) examined the hydrodynamics of reactive and non-reactive distillation systems and evaluated the accuracy of computational fluid dynamics (CFD) simulations used to predict the flow behavior in tray systems. They studied the 25th tray in the methyl acetate production process in the reactive distillation system and used Aspen Plus V9.0 to simulate the tray's net liquid height as a function of tray shape and operating circumstances. For the manufacture of methyl acetate, they employed a 38-stage reactive distillation design and contrasted the outcomes with the outputs that were already produced. There were minor differences amongst the outcomes, but overall there was a fair amount of agreement. They contended that the

observed inconsistencies were caused by mass transfer effects and the turbulence-chemistry relationship. They demonstrated how these variables depend on flow behavior by visualizing the distributions of mole fractions, temperature, and reaction rates within particular ranges for the methyl acetate synthesis process using CFD simulations. Additionally, they examined the effects of superficial velocity, noting that as superficial velocity increased, so did the amplitude. They concluded that methyl acetate production was highly dependent on this variable, with an optimal value of approximately 0.6 m/s. In other words, the maximum product yield for methyl acetate and water was achieved at a superficial velocity of 0.6 m/s.

Sarma et al. (2016) used Aspen Plus software to control a reactive distillation column for maintaining the desired product purity. They employed a robust control scheme consisting of pressure, temperature, flow, composition, and reflux controllers. They found that the control structure applied for the design and control of the reactive distillation column in the methyl acetate system provided effective control, even in scenarios requiring high product purity. Due to the lack of direct control over product compositions, they reported that the setpoint of the temperature controller and the reflux ratio should be adjusted to overcome worst-case conditions. They suggested further studies by applying more advanced control systems, such as model predictive control (MPC).

2. Materials and Methods

2.1 Reactive distillation

Reactive distillation is a process in which the chemical reaction and the separation of products occur simultaneously within a single unit. The separation, purification, and reaction of the products happen concurrently in one unit. The design of reactive distillation columns is a complex process due to the interaction of numerous variables (Towler and Sinnott, 2008).

Table 1. Comparison of batch, semi-batch, and continuous distillation columns

Properties	Batch	Semi-batch	Continuous
Investment	Low	Medium	High
Flexibility	More flexible	More flexible	Less flexible
Single column for ternary mixing	Yes	Yes	No
Heat integration	No	No	Yes
Automatic control	Rarely	Partially	Oftenly
Efficiency	Low	Medium	High

In the past, reactive distillation has been successfully employed and investigated for a variety of reactions, including etherification, esterification, hydrogenation, hydrodesulfurization, and polymerization. The synthesis of methyl acetate via reactive distillation has been the subject of numerous studies. Methyl acetate is used as an intermediate in the production of various polyesters, including photographic film base, cellulose acetate, tenite cellulosic plastics, and estrone acetate. Table 1 provides a comparison of batch, semi-batch, and continuous distillation columns (Aqar, 2018).

2.2 Operating parameters of the reactive distillation process

The reactive distillation column consists of three sections: the stripping section, the reaction section, and the enriching section. Figure 1 shows the process flow diagram of the reactive distillation system. As depicted in the figure, acetic acid and methanol are continuously fed into the reaction section, and methyl acetate is obtained as the top product.

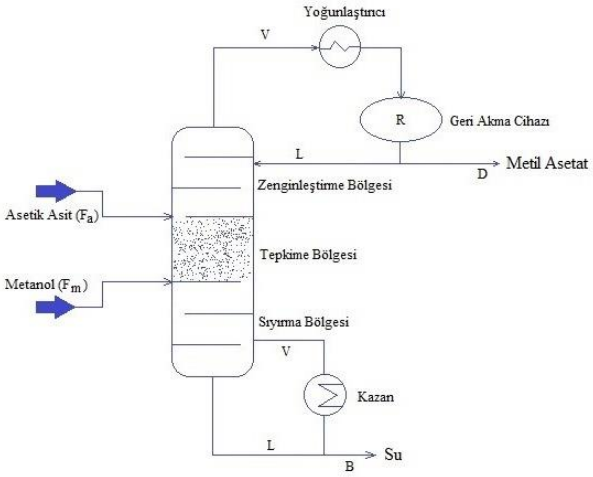

Figure 1. Process flow diagram of the reactive distillation system

In the design of the reactive distillation column, key variables that are considered crucial for the intended production process are selected based on design principles. These variables directly or indirectly affect the production process, and therefore, the most effective variables are determined by considering investment and operating costs. The design variables are listed below:

- Column operation mode (batch, semi-batch, continuous),
- Column type (packed or tray, fluidized bed),
- Properties of packing materials (in packed columns),
- Number of trays in the column,
- Physical properties of the column (pressure, temperature, etc.),
- Type of catalyst selected,
- Relative volatilities of the chemicals,
- Feed ratios and flow rates of the chemicals,
- Reflux ratio,
- Reboiler duty.

To better understand the interactions between the components, it is useful to know their physical properties. Table 2 provides some physical properties of the components (Yıldırım, 2020).

Table 2. Physically properties

Component	Molecule formule	Molecule weight (g/mol)	Boiling point (°C)
Acetic acide	$C_2H_4O_2$	60.05	118
Methanol	CH_4O	32.04	64.7
Methyl acetate	$C_3H_6O_2$	74.08	57
Water	H_2O	18.01	100

2.3 Process Design Using Chemcad

The esterification reaction between methanol and acetic acid leads to the production of methyl acetate as a product. In this theoretical study, simulations were performed using Chemcad version 6.5.7, a process simulation software developed by Chemstations. The focus was on simulating different operating conditions in a reactive distillation column where both the reaction and separation occur simultaneously. The primary goal of the design was to create an efficient system that ensures maximum yield with minimum resource utilization, balancing production costs and investment requirements. The system model for the simulation experiments consisted of feed lines for methanol and acetic acid, a reboiler, condenser, reflux unit, and collection lines for both top and bottom products. The process flow diagram for the reactive distillation column was designed in Chemcad and is shown in Figure 2.

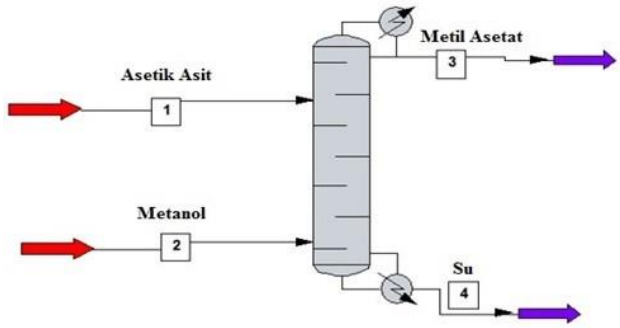

Figure 2. The process flow diagram for the reactive distillation column

The simulation of the reactive distillation column in Chemcad enabled the separation of methyl acetate as the top product and water as the bottom product through chemical reactions.

The elements of the reactive distillation column, along with their properties and the connections between the input-output streams, were defined in the software. Scanning was performed to determine which variables had the most significant impact on the efficiency of the reaction and distillation processes. Based on the literature, key design details were established, and simulation trials were evaluated to determine the operating ranges. The resulting values were incorporated into the system as the working principles of the simulation. Critical design elements, such as operating pressure, the number of stages, feed stages for acetic acid and methanol, and reflux ratio, were defined within the model, and the overall framework of the designed system was established. Table 3 provides numerical values for the characteristics of the reactive distillation column.

Table 3. The properties of reactive distillation column

Properties	Values
Column tray numbers	20
Acetic acid feeding stage	10
Methanol feeding stage	14
Range of reactive stage	10-14
Column pressure (kPa)	101

Simulating the reactive distillation column provides several advantages, including time and resource savings, the determination of the appropriate number of trays, the selection of optimal feed stages, obtaining high-purity chemicals, identifying priority reaction variables with the greatest impact on results, establishing the best operating conditions for the column, and improving process design to increase production efficiency (Ersingün, 2019).

3. Results and Discussions

The methods developed for reactive distillation were applied in theoretical studies using Chemcad and experimental design programs. Steady-state experiments were conducted in Chemcad for different input variables, and the working ranges were determined as follows: feed rate between 2.5-5, reflux ratio between 1-1.5, and feed temperature between 30-60 °C.

The simulation results revealed the temperature profile along the column. As expected, the temperature decreased from the reboiler to the condenser, but increased in the reaction zone (between stages 10 and 14) due to the exothermic nature of the reaction. The mass flow rates of the total vapor and total liquid phases throughout the column are presented in Table 4. It was observed that both liquid and vapor phase values significantly increased in the reaction zone.

Table 4. The mass flow rates of the total vapor and total liquid phases

Tray number	Temperature (˚C)	Liquid phase (kg/s)	Vapor phase (kg/s)
1	120.4	142.82	-
2	122.7	136.27	238.03
3	121.2	132.21	231.48
4	120.7	131.25	227.42
5	120.6	131.06	226.46
6	120.6	131.02	226.27
7	120.6	131.02	226.23
8	120.6	131.01	226.23
9	120.6	131.01	226.22
10	120.6	1418.20	226.22
11	113.2	1282.27	704.73
12	107.6	1197.69	568.80
13	103.1	1134.91	484.22
14	98.7	1247.25	421.44
15	105.1	1343.94	469.71
16	110.5	1431.42	566.40
17	114.0	1493.15	653.87
18	116.0	1530.74	715.60
19	117.1	1552.28	753.19
20	117.7	-	774.73

Table 5. Physical properties of the liquid phase

Tray number	Mass flow rate (kg/s)	Density (kg/m³)	Viscosity (cP)
1	143	593.97	0.1939
2	136	593.24	0.1945
3	132	596.51	0.1971
4	131	597.12	0.1978
5	131	597.24	0.1979
6	131	597.27	0.1980
7	131	597.27	0.1980
8	131	597.27	0.1980
9	131	597.27	0.1980
10	1418	597.27	0.1980
11	1282	606.74	0.2094
12	1198	613.77	0.2185
13	1135	619.47	0.2263
14	1247	625.14	0.2343
15	1344	616.88	0.2227
16	1431	610.09	0.2137
17	1493	605.71	0.2081
18	1531	603.22	0.2050
19	1552	601.86	0.2034
20	778	601.11	0.2035

Table 5 shows the numerical values for the physical properties of the liquid phase, including mass flow rates, density, and viscosity. Similarly, Table 6 presents the physical properties of the vapor phase, including mass and volumetric flow rates, viscosity, thermal conductivity, and surface tension.

Table 6. Physical properties of the vapor phase

Tray number	Mass flow rate (kg/s)	Density (kg/m³)	Viscosity (cP)
1	0	0	0
2	238	3.4980	0.0079
3	231	3.3187	0.0080
4	227	3.2755	0.0080
5	226	3.2669	0.0080
6	226	3.2653	0.0080
7	226	3.2650	0.0080
8	226	3.2649	0.0080
9	226	3.2649	0.0080
10	226	3.2649	0.0080
11	705	2.7149	0.0085
12	569	2.3991	0.0089
13	484	2.1854	0.0092
14	421	2.0060	0.0092
15	470	2.2782	0.0095
16	566	2.5566	0.0091
17	654	2.7671	0.0087
18	716	2.8996	0.0085
19	753	2.9766	0.0083
20	775	3.0203	0.0082

Figure 3 shows the temperature changes along the column. The changes in total vapor and total liquid phase balances during the distillation process are shown in Figures 4 and 5, respectively. As seen from these profiles, total vapor and liquid phases decreased from the reboiler to the condenser, while a noticeable increase in mass flow rates was observed in the reaction zone due to the expected rise in temperature.

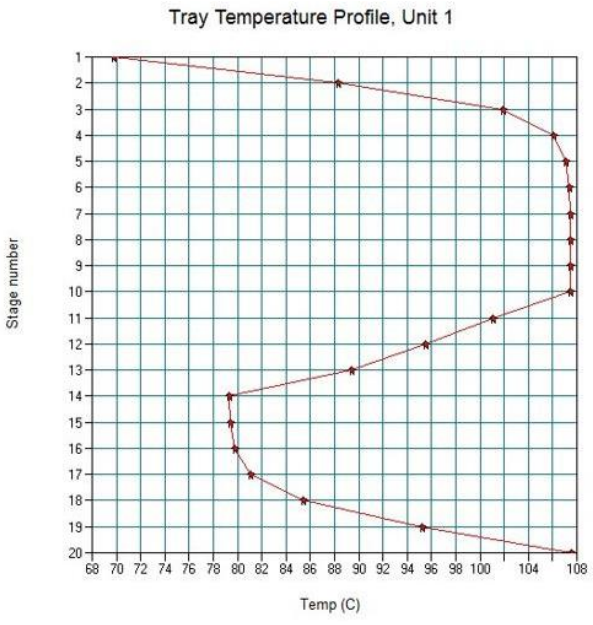

Figure 3. Temperature changes along the column

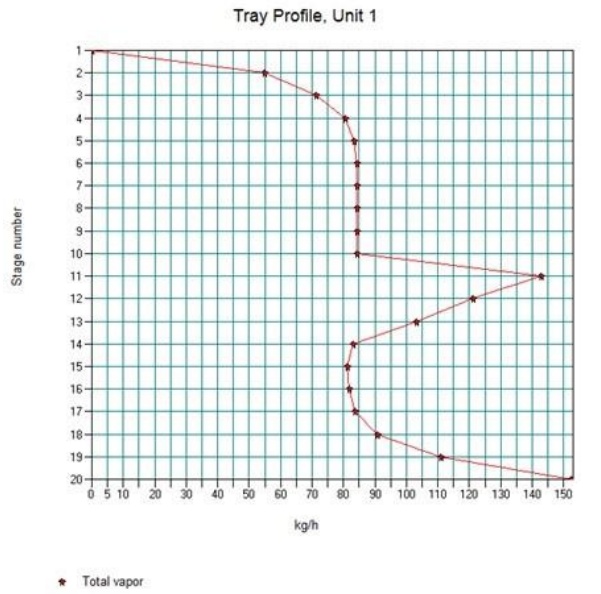

Figure 4. The changes in total vapor balances during the distillation process

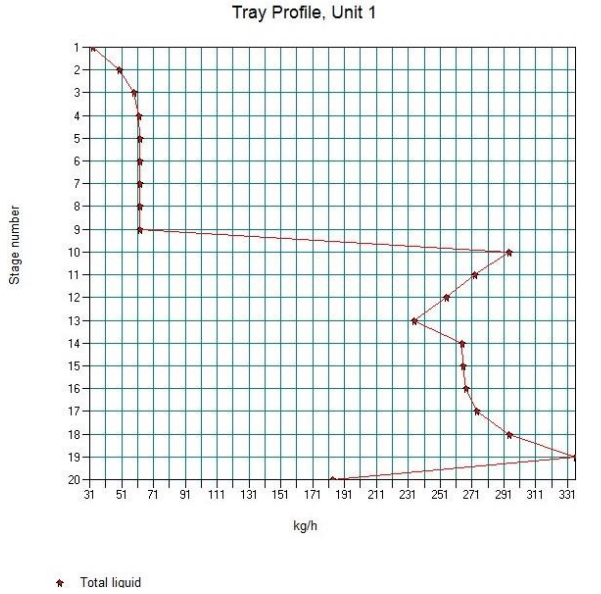

Figure 5. The changes in total liquid balances during the distillation process

4. Conclusions

The reactive distillation system is an integrated process where both the reaction and distillation occur together. Compared to traditional distillation methods, it has been determined that reactive distillation provides higher product yield. In this study, the effects of operating parameters—such as feed rate, reflux ratio, and feed temperature—on the yield of methyl acetate were observed in the simulated reactive distillation column.

As emphasized in the study by Ersingün (2019), esterification reactions are equilibrium-limited, and after the reaction, a series of separation steps is typically required. Reactive distillation eliminates this problem. By combining the chemical reaction and separation processes in a single unit, the equilibrium is shifted toward product formation, thereby increasing conversion and selectivity.

Similar to the findings of Muthia et al. (2019), the reactive distillation process achieved cost reductions and energy savings, with quick results regarding optimum feed conditions and reduced energy requirements (i.e., lower reflux ratio).

For the methyl acetate production process, the dependence of mole fractions, temperature, and reaction rate distributions on flow behavior was demonstrated. After the flow diagram structure was established, it was determined that a step-by-step approach was necessary to minimize total annual costs (Tang et al., 2005).

Declaration of Ethical Standards

The authors declare that they comply with all ethical standards.

This study was carried out by Alper GÜNAY under the supervision of Assist. Prof. İsmail BAYRAM. It is derived from the master of thesis titled "Optimization of operating conditions using design expert methodology with dynamic simulation of reactive distillation column".

Credit Authorship Contribution Statement

Author 1: Conceptualization, Methodology, Validation, Resources, Writing – review and editing, Visualization, Supervision.
Author 2: Methodology, Software, Writing – original draft.

Declaration of Competing Interest

The authors have no conflicts of interest to declare regarding the content of this article.

Data Availability

All data generated or analyzed during this study are included in this published article.

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