



Endüstriyel Atık Gazlardan Karbon Dioksitin Yakalanması

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Öz

Bu çalışmada, Batman ve Siirt illeri arasında bulunan bir endüstriyel üretim tesisinden salınan CO₂'nin uygun çözümler kullanılarak yakalanması, Aspen Plus simülasyonu kullanılarak modellenmiştir. Çalışmada, CO₂ yakalama ajanı olarak metildietanolamin (MDEA) çözültisi seçilmiştir. Proses tasarımında emiciler, sıyırıcılar, ısı eşanjörleri, flaş buharlaştırıcılar ve devridaim döngüleri kullanılmıştır; farklı besleme hızları ve tepsi sayıları test edilmiştir. İlk aşamada, 400 ton/saat besleme çözültisi ile CO₂'nin sadece %47'si yakalanabilmiştir. Ancak, çözülti akış hızı 832 ton/saate çıkarılınca, besleme akışında bulunan 76 ton/saat CO₂'nin yaklaşık 72,14 ton/saati (%95) başarıyla yakalanmıştır. Ayrıca, başlangıçta hem emici hem de sıyırıcıda 30 olarak ayarlanan tepsi sayısının, performansta önemli bir değişiklik olmaksızın 21'e düşürülebileceği ve böylece işlemin maliyet etkinliğinin artırılacağı gözlemlenmiştir. Elde edilen sonuçlar, endüstriyel tesislerde MDEA çözültileri kullanılarak CO₂ yakalama yönteminin yüksek verimlilik sağladığını göstermektedir. Ancak, CO₂'nin sadece yakalanması değil, kimyasal/yakıt üretiminde de kullanılması gerektiği vurgulanmaktadır. Bu tür teknolojilerin yaygın olarak benimsenmesi, Türkiye'nin gelecekteki iklim hedeflerine ulaşmasına önemli ölçüde katkıda bulunacaktır.

Anahtar kelimeler: Aspen plus, Karbon yakalama, Endüstriyel kirlilik, MDEA

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Capturing Carbon Dioxide from Industrial Waste Gases

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Abstract

In this study, the capture of CO₂ released from an industrial production facility located between the provinces of Batman and Siirt using suitable solutions was modelled using the Aspen Plus simulation. In the study, a methyldiethanolamine (MDEA) solution was chosen as the CO₂ capture agent. The process design utilized absorbers, strippers, heat exchangers, flash evaporators, and recirculation loops; different feed rates and tray counts were tested. In the first stage, only 47% of the CO₂ could be captured with a feed solution of 400 t/h. However, by increasing the solution flow rate to 832 t/h, approximately 72.14 t/h (95%) of the 76 t/h of CO₂ present in the feed stream was successfully captured. Furthermore, it was observed that the number of trays, initially set at 30 in both the absorber and stripper, could be reduced to 21 without any significant change in performance, thereby increasing the cost-effectiveness of the process. The results obtained demonstrate that the CO₂ capture method using MDEA solutions in industrial facilities provides high efficiency. However, it is emphasized that CO₂ should not only be captured but also utilized in chemical/fuel production. The widespread adoption of such technologies will significantly contribute to Turkey's achievement of future climate goals.

Keywords: Aspen plus, Carbon capture, Industrial pollution, MDEA

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1. Introduction

With the Industrial Revolution, the intensive use of fossil fuels rapidly increased the amount of greenhouse gases in the atmosphere, and carbon dioxide (CO₂) emissions in particular became the primary driver of climate change. Globally, CO₂ emissions from the energy sector reached a historic peak of 36.8 gigatons in 2022, and this increase seriously threatens the goal of limiting global warming to 1.5 °C, as stated in the International Panel on Climate Change's (IPCC) sixth assessment report [1]. The increase in atmospheric CO₂ not only causes temperature increases but also triggers wide-ranging problems such as rising sea levels, ecosystem degradation, and intensification of extreme weather events [2]. In this context, Carbon Capture, Utilization, and Storage (CCUS) technologies stand out as one of the critical solutions for mitigating the effects of climate change. CCUS encompasses the processes of capturing CO₂ at its source in industrial facilities or during energy production, transporting it using appropriate technologies, utilizing it in different areas, or storing it long-term in safe geological reservoirs [3]. The sub-branches of the technology, Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU), enable both the reduction of emissions and the conversion of carbon into an economic input. Notably, at the 28th meeting of the conference of the parties' summit held in Dubai in 2023, the necessity of a gradual phase-out of fossil fuels was emphasized, and it was acknowledged that the application of CCS technologies is inevitable, particularly in heavy industries where no alternatives exist.

The advantages and disadvantages of different carbon capture technologies have also been discussed in detail in the international literature. For example, although post-combustion CO₂ capture technologies offer high efficiency, the most significant disadvantage is the increase in solvent consumption and costs when working with low-concentration gases [4, 5, 6]. Pre-combustion CO₂ capture, although offering capture efficiencies above 90%, has limited application due to high energy consumption and difficulties in integrating it into existing facilities [4, 7, 8, 9]. Oxy-fuel combustion technology is a promising option with capture rates of up to 98%, but it has economic limitations due to the need for high-purity oxygen and durable materials [10]. In addition, bioenergy with carbon capture and storage (BECCS) stands out among "negative emission technologies" and is considered by the IPCC to be an integral part of carbon-neutral scenarios beyond 2050 [11]. The utilization of captured CO₂ is a critical factor for the economic sustainability of the technology. Today, CO₂ can be used in methanol and synthetic fuel production, polymer synthesis, construction materials such as cement and aggregates, fertilizer production in agriculture, and even in refrigerants [12]. These versatile applications transform carbon capture investments from a mere environmental necessity into an economic opportunity.

Academic and industrial studies conducted in Turkey have yielded important findings regarding the integration of CO₂ capture technologies into local conditions. This study models the CO₂ released from an industrial production facility between the provinces of Batman and Siirt using Aspen Plus software and examines its absorption with methyldiethanolamine (MDEA) solutions, demonstrating a high rate of CO₂ separability. Thus, it offers a feasible solution at the local level and provides a technical contribution to Turkey's 2053 net-zero targets.

2. Methodology

Aspen Plus is a chemical process simulator in the chemical engineering market, is a software that enables users to create a process model and then simulate it using equations or mathematical calculations to measure the relationship between two or more variables. In addition to advantages such as designing new processes and improving existing ones, it maximizes profit by combining them with cost-saving workflows. Another advantage is that the thermodynamic properties used in modelling are stored in a database within the program, which includes types and pure/binary selection parameters.

2.1 Simulation process main inputs

Various CO₂ scrubbers are available to prevent the release of CO₂ emitted from any industrial facility into the environment. Among these scrubbers, MDEA plays an important role. In this study, MDEA is used as a

CO₂ scrubber to eliminate CO₂ emissions from an industrial facility. The CO₂ amount of an industrial facility near the Batman and Siirt region is approximately 75 t/h, and its emission is modelled using the Aspen Plus simulation program. The temperature and pressure of CO₂ are taken as 40 °C and 27 bar, respectively. The components in the feed gas are used in the simulation in terms of molar fraction: H₂O (0.002), CO₂ (0.189), H₂ (0.745), CH₄ (0.058), CO (0.004), and N₂ (0.002). The Redlich-Kwong physical property package with the NRTL electrolyte is used in the simulation, and the purpose of using this fluid package is due to the dissociation of the components in the CO₂-water mixture into hydronium, carbonate, and bicarbonate ions [13-15]. A pure solution containing equal moles of H₂O and MDEA is fed at 600 t/h from the top of the absorber, while the feed gas solution is fed into the system from the bottom of the absorber. The pressures and temperatures of both feed streams are assumed to be the same. This simulation includes the following six equilibrium reactions:



2.2 Process flow diagram description

The components in the process flow diagram designed for CO₂ capture consist of an absorber, heat exchanger, stripper, cooler, flash evaporator, mixer, and pump system. First, the feed gas containing CO₂ is fed into the stripper at 40 °C and 27 bar pressure with a pure MDEA solution. The number of absorber stages is taken as 15, and the condenser and reboiler sections are neglected in the simulation. The pure solution enters the absorber at the 1st stage, while the feed gas enters at the 15th stage. The efficiency/effectiveness of the liquid-vapor mixture in the absorber is taken as Murphree efficiency 0.4. In the simulation, it is assumed that only MDEA and CO₂ react, and hydrogen sulphide does not react in the system. Using the “Design Specs” feature in the simulation, the ratio of CO₂ in the H₂ gas in the absorber top stream to the CO₂ in the feed stream is set to 0.05. The CO₂-rich absorber outlet stream is then heated to 110 °C using a heat exchanger. The heated rich solution is fed to the stripper for CO₂ gas separation. The number of stripper stages is assumed to be 21, the boiling rate is 0.2, and the reflux rate is 0.1. The Murphree efficiency in the stripper is assumed to be the same as the absorber efficiency. In the stripper's top stream, CO₂, H₂O, and a certain amount of CH₄ are cooled to 10 °C via a heat exchanger before being fed to the flash evaporator. As CO₂ exits the flash evaporator from the top stream, H₂O leaves the system from the bottom stream of the flash evaporator. The H₂O leaving the flash evaporator and the stripper bottom stream are fed back into the system and supplied to the absorber inlet stream with the make-up amount of MDEA using a mixer. The “Calculator Block” is used to calculate the amount of H₂O and MDEA lost in the upper stream of the flash evaporator, the amount of H₂O and MDEA lost in the upper stream section of the absorber component, the amount of H₂O in the feed stream, and the required amount of H₂O and MDEA in the make-up stream. After the “Calculator Block” process is completed, a pump compatible with the liquid-vapor flow with a discharge pressure of 40 bar is added to the mixer outlet flow. After this process, the pure solution flow initially added to the absorber in the simulation is cancelled and replaced with the pump outlet flow added to the absorber, and the inlet flow rate is adjusted using the “Design Specs” feature. The general process flow diagram of CO₂ using MDEA is shown in Figure 1.

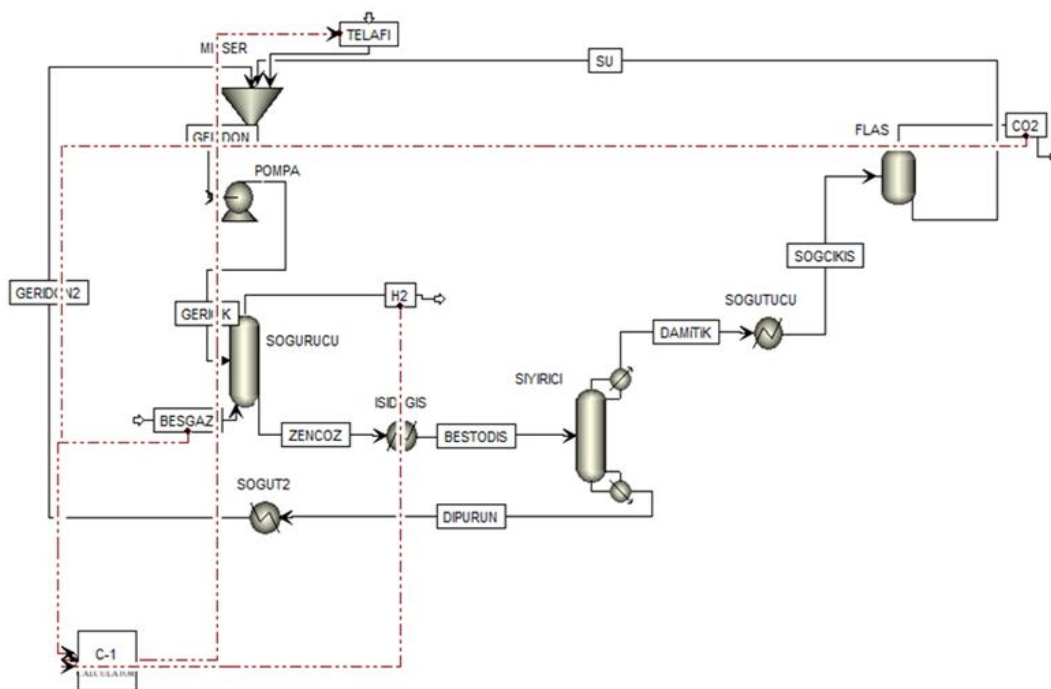


Figure 1. Process flow diagram for CO₂ capture using MDEA

3. Results and Discussion

When the pure solution enters the absorber from the 1st tray, it is assumed that the feed gas containing CO₂ enters from the 15th tray. While the residence times of the liquid and gas phases in the absorber are calculated as 5 s per tray for the liquid, increasing the number of iterations in the simulation program from 25 to 200 reveals that approximately 47% of the 76,000 kg/h CO₂ feed is separated in the absorber stream. However, since the objective of this simulation is to achieve CO₂ separation from the feed gas between 95% and 97%, the amount of pure solution must be increased. Using the “Design Specs” feature, it is seen that the amount of pure solution, initially entered as 400 t/h, should be used as 832 t/h. When 832 t/h of MDEA is used in the simulation, it is seen that approximately 72.14 t/h of CO₂, or approximately 95%, is removed from the feed gas in the CO₂ outlet stream, which was initially approximately 76 t/h. When the CO₂-rich solution from the absorber bottom outlet enters the stripper after exiting the heater, the stripper tray number is initially set to 30. In the simulation, the iteration number is increased from 25 to 200, as in the absorber unit, and the simulation is observed to run correctly. The temperature on the 1st tray of the stripper unit is calculated as 59.6 °C, while the temperature on the 30th tray is calculated as 106.2 °C. A heat exchanger, which acts as a cooler, is added to reduce the temperature in the distillation unit of the stripper to 10 °C. It is assumed that there is no pressure drop in the heat exchanger. CO₂ is separated from H₂O in the distillate stream of the stripper by means of a flash evaporator. 0.996 of the CO₂ and H₂O mixture coming out of the cooler is separated in the flash evaporator. Thus, high-purity CO₂ is separated from the upper stream of the flash evaporator. Most of the H₂O separated from the mixture in the lower stream enters the mixer before entering the absorber via the recirculation stream. The MDEA and H₂O separated in the lower stream of the stripper are sent to the mixer for re-evaluation. At the start of the simulation, instead of a pure solution containing MDEA and H₂O, the return streams and the make-up stream are mixed in the mixer and connected to the absorber inlet stream at the end of the simulation. Only 0.36% H₂O and 1.46% MDEA are lost as H₂O and MDEA, respectively, from the absorber outlet stream.

Initially, when the component profile “Column Design” in Aspen Plus was selected with 30 trays for the absorber and stripper, (component profiles) in Aspen Plus, it was observed that there was not much change in the separation of MDEA composition in the stripper after 21 trays. Therefore, the number of trays was changed to 21 in both the absorber and stripper to reduce costs. Figure 2 shows the composition

change with the number of trays.

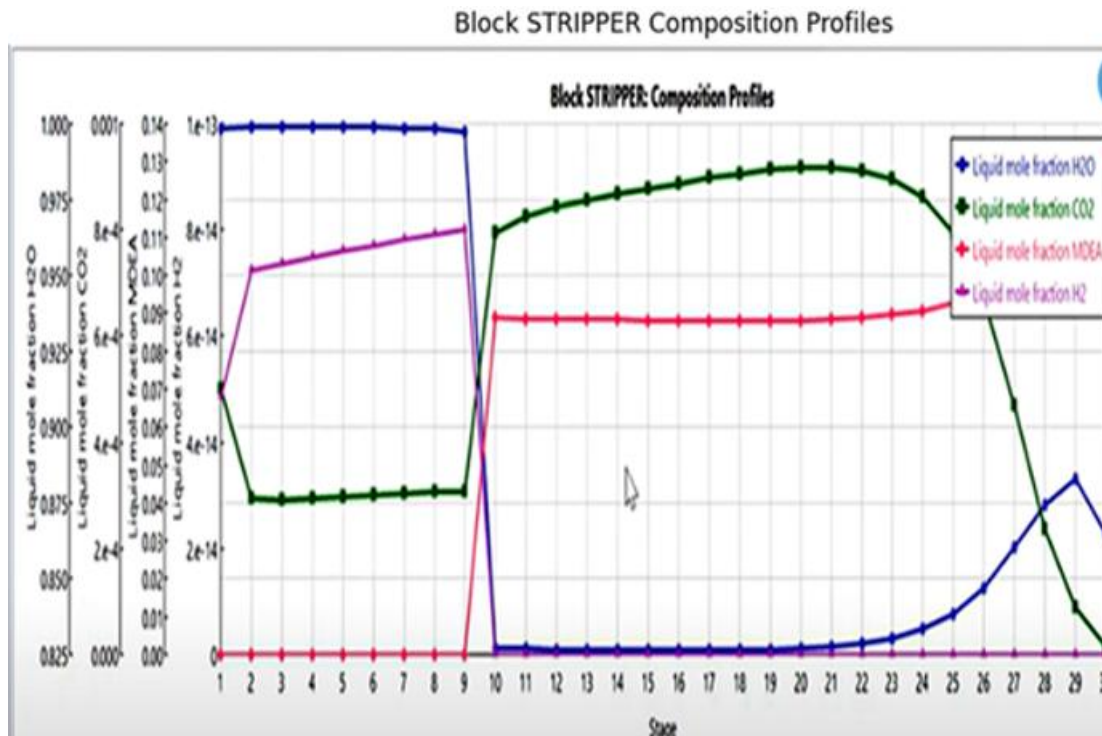


Figure 2. Composition change with the number of trays.

Compensation H₂O (MAKW) = Amount of H₂O in the CO₂ stream (WCO₂) + Amount of H₂O in the H₂ stream (WH₂) – Amount of H₂O in the feed stream (WF) (7)

Compensation MDEA (MAKM) = Amount of MDEA in the CO₂ stream (WCO₂) + Amount of MDEA in the H₂ stream (WH₂) (8)

Additionally, the Fortran codes in the simulation are provided as follows. The Figure 3 shows Fortran codes of H₂O and MDEA calculations.

```

Enter executable Fortran statements
MAKW=WCO2+WH2-WF
MAKM=MCO2+MH2
    
```

Figure 3. Calculation of H₂O and MDEA quantities in Fortran

The H₂O and MDEA calculated in Fortran for the make-up flow are 814.41 kg/h and 1.50 kg/h, respectively. Pump equipment is also required at the outlet of the mixer flow to feed the absorber. The required discharge pressure is taken as 40 bar. The flow brought to the desired pressure is included in the simulation flow instead of the pure solution to the absorber, and the absorption of CO₂ with MDEA is completed. The mass flow data for all flows are given in Table 1 below.

Table 1. All flows in the process diagram used for CO₂ absorption

Units	BESGAZ	BESTODIS	CO ₂	DIPURN	GRCK	GRDN	GRD2	H2	SGCK	SU	TLAFİ	ZENÇZ	
Mass Flows	kg/hr	100,000	925,619	73727.7	843650	852,706	852,706	843,650	27,087.5	81,968	824,034	814,525	925,619
H ₂ O	kg/hr	329.97	396,079	197.66	411,107	420,089	420,089	411,103	944.24	83,853	8187.64	812.99	391,334
MDEA	kg/hr	0	287306	0	425,664	424,428	424,406	424,547	1.50	0,0003	0,0003	1.502	235,384
H ₂ S	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
CO ₂	kg/hr	75,832.6	14979.5	72136	147,941	0.204	0.194	0.191	3796.57	72072.2	0	0	3388.5
HCO ₃ ⁻	kg/hr	0	800,304	0	2243.51	1745.23	1733.98	1705.07	0	1477.4	0	0	95569.8
MDEA ⁺	kg/hr	0	163,780	0	4582.92	5833.57	5855.82	5709.45	0	2869.4	0,0027	0,0027	1964.75
CO ₃ ²⁻	kg/hr	0	1538.28	0	33.25	593.87	605,134	582.81	0	0	0	0	2060.62
HS ⁻	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
S ⁻²	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
H ₃ O ⁺	kg/hr	0	0,00039	0	0	0	0	0	0	0,0019	0	0	0,0035
OH ⁻	kg/hr	0	0,315	0	4.39	2.48	2.43	2.43	0	0	0	0	0,2492
H ₂	kg/hr	13,710	0,011	0,011	0	0	0	0	13,710	0,012	0	0	0,012
CH ₄	kg/hr	8434,23	1381.9	1369.12	0	12.78	0	0	7125.11	1381.9	0	0	1381.9
CO	kg/hr	1022.81	76,51	16.49	0	0,023	0,023	0	1006.32	1651.54	0	0	1651.54
N ₂	kg/hr	511.44	7.72	7.72	0	0,009	0,009	0	503.75	7.72	0	0	7.72

4. Conclusions

The objective of this study was to use appropriate solutions to absorb the CO₂ emitted at an industrial production center situated between the provinces of Batman and Siirt. It was found that 47% of the CO₂ in the system was extracted from the feed when the residence periods of the liquid and gas phases in the absorber were computed as 5 seconds per shelf for the liquid. When the pure solution feed rate was raised from 400 t/h to 832 t/h in the simulation, it was found that 72.14 t/h of the 76 t/h of CO₂ in the outlet stream was removed from the feed gas, indicating that roughly 95% of the CO₂ was removed from the system. This is because 95–97% separation of CO₂ is desired. Additionally, even though there were 30 trays in the original simulation, it was found that the software did not appreciably alter the separation of the MDEA composition in the stripper after 21 trays. Therefore, in order to reduce capital costs on the absorber and stripper, 21 trays were chosen. It is known that the gas released into the atmosphere by living organisms constitutes a small fraction compared to the CO₂ gas emitted by factories or manufacturing plants. Therefore, it is crucial to carefully examine and conduct research and studies aimed at reducing CO₂ emissions from production sources. CO₂ is crucial not only because it plays a key role in the photosynthesis process of plants but also because it ensures the existence of life on Earth by affecting the average temperature in the atmosphere. While it is a necessary component, its excess also causes damage to the global ecosystem.

5. Author Contribution Statement

Özcan BAŞARAN: Formal analysis, Investigation, Resources Formal analysis, Investigation, Methodology, Writing—original draft Yavuz KIRIM: Conceptualization, Supervision, Validation, Visualization, Writing – review & editing

6. Ethics Committee Approval and Conflict of Interest

“There is no conflict of interest with any person/institution in the prepared article. Additionally, ethics committee approval is not required for this study.”

7. Ethical Statement Regarding the Use of Artificial Intelligence

No artificial intelligence-based tools or applications were used in the preparation of this study. The entire content of the study was produced by the author in accordance with scientific research methods and academic ethical principles

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