

Kinetic Study Of CO₂ Adsorption In Two-Stage Biogas Purification Using Activated Natural Zeolite

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Abstract—The presence of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) in raw biogas reduces its combustion efficiency and poses risks to system durability. This study investigates the kinetic performance of a two-stage biogas purification system using chemically activated natural zeolite. The first stage utilized zeolite activated with 20% potassium hydroxide (KOH), while the second stage employed zeolite activated with 3 M hydrochloric acid (HCl). Experimental results demonstrated a substantial improvement in methane (CH₄) concentration from approximately 60% to 95% after purification, alongside a significant reduction in CO₂ (from 40% to 15%) and near-complete elimination of H₂S (from ~400 ppm to ~0 ppm). A three-dimensional kinetic analysis revealed that CO₂ adsorption efficiency peaked at nearly 100% within the first 60 seconds but gradually declined to around 70% at 300 seconds, indicating adsorbent saturation. The effectiveness of the dual-stage approach is attributed to the synergistic action of basic and acidic activations, which provide complementary adsorption environments for CO₂ and H₂S. These findings confirm that sequential purification using activated zeolite offers a promising, low-cost solution for enhancing biomethane quality, particularly for decentralized or small-scale applications.

Keywords— biogas upgrading, carbon dioxide adsorption, dual-stage purification, natural zeolite

I. INTRODUCTION

The growing global demand for renewable and sustainable energy has intensified interest in biogas as a viable alternative to fossil fuels. Biogas, produced through anaerobic digestion (AD) of organic matter such as livestock manure, agricultural waste, and food residues, primarily consists of methane (CH₄), carbon dioxide (CO₂), and trace amounts of hydrogen sulfide (H₂S), moisture, and other minor components. Among these, methane is the desired combustible fraction, whereas CO₂ and H₂S are considered undesirable impurities. The presence of these non-combustible and corrosive components significantly reduces the calorific value of raw biogas, limits its combustion efficiency, and contributes to corrosion-related damage in gas engines, pipelines, and storage systems [1,2]. Moreover, the release of H₂S during combustion can lead to the formation of sulfur dioxide (SO₂), which is harmful to the environment and human health.

To convert raw biogas into biomethane—a higher-purity fuel that meets pipeline or vehicle-grade standards—several upgrading technologies have been developed, including water scrubbing, pressure swing adsorption (PSA), cryogenic separation, membrane separation, and chemical or physical absorption [3,4]. While these methods vary in performance and cost, many are capital- and energy-intensive, making them less feasible for small-scale or decentralized applications. As an alternative, adsorption-based techniques using solid adsorbents have emerged as promising options, particularly in rural or low-resource contexts.

Natural zeolite is one of the most widely studied and utilized adsorbents in biogas purification. Its abundant availability, low cost, chemical stability, and high cation-exchange capacity make it an attractive material for selective removal of CO₂ and H₂S [5,6]. Clinoptilolite-type zeolites, in particular, offer a well-defined microporous structure with a high affinity for polar and acidic gases. Furthermore, the adsorption efficiency of natural zeolite can be significantly enhanced through chemical activation. Treatment with strong acids (e.g., HCl) or bases (e.g., KOH) alters the surface chemistry, increases the surface area, improves pore accessibility, and introduces or exposes functional groups that serve as active sites for gas adsorption [7].

Previous studies have typically focused on the use of single-stage adsorption systems, wherein natural zeolite is activated either with a base or an acid and used alone for the removal of CO₂ or H₂S [8,9]. While these methods have shown reasonable performance, the adsorption capacity is often limited by the chemical specificity of the adsorbent and the rapid saturation of active sites. To address this limitation, a dual-stage adsorption configuration is proposed, where biogas sequentially passes through two distinct columns filled with zeolite activated by different chemical agents. This approach aims to capitalize on the complementary properties of basic and acidic activation to optimize the removal of multiple contaminants simultaneously.

Despite the theoretical promise of this dual-stage configuration, studies on the adsorption kinetics in such systems remain scarce. Understanding the time-dependent adsorption behavior is crucial for predicting the operational life of the adsorbent, determining regeneration cycles, and designing efficient systems.

The present study investigates the kinetics of CO₂ adsorption in a two-stage biogas purification system using natural zeolite activated sequentially with potassium hydroxide (20% KOH) and hydrochloric acid (3 M HCl). The goal is to evaluate the dynamic removal efficiency of CO₂ over time and analyze the saturation behavior of the adsorbents under continuous flow conditions. This study is expected to provide new insights into the feasibility and optimization of chemically activated zeolite for decentralized biogas upgrading applications.

II. EXPERIMENTAL DESIGN

A. Materials

Natural zeolite used in this study was obtained from Lombok Island, Indonesia. The raw zeolite was initially crushed and sieved to obtain uniform particle size, with a final mesh size of 10 to ensure consistent packing in the adsorption column. The native clinoptilolite-rich zeolite was chosen due to its high cation exchange capacity and microporous structure, which are favorable for gas adsorption processes.

B. Zeolite Activation Procedure

To enhance the adsorptive properties of the natural zeolite, chemical activation was performed using potassium hydroxide (KOH) and hydrochloric acid (HCl). The zeolite was divided into two batches: one soaked in KOH solution and the other in HCl solution. Each batch underwent impregnation at a 1:2 mass-to-volume ratio with activating agents at concentrations of 10%, 15%, and 20% for KOH, and 3 M for HCl. The soaking duration was maintained for several hours to ensure optimal interaction and surface modification. Post-treatment, the zeolites were rinsed with deionized water until neutral pH was achieved and subsequently dried using a desiccator. Final physical activation was conducted by heating the samples at 300 °C for 3 hours in a muffle furnace to improve pore accessibility and remove residual moisture.

C. Biogas Generation and Storage

Biogas was produced through anaerobic digestion using cow manure collected from local smallholder farms. The digestion process was carried out in a 3 m³ laboratory-scale digester with a 1:1 water-to-manure ratio, supplemented by 200 mL of EM-4

(effective microorganism) to accelerate microbial activity. The biogas generated was stored in a dedicated gas reservoir (4 m³ capacity), equipped with a manometer and drain valves to monitor and regulate internal pressure and gas flow. A secondary reservoir was prepared to collect purified biogas after the adsorption process.

D. Two-Stage Biogas Purification and CO₂ Adsorption Kinetics Monitoring

The purification process was carried out using a dual-stage fixed-bed column system packed sequentially with KOH-activated and HCl-activated zeolite. Each stage contained 200 g of activated zeolite with a column diameter-to-height ratio of 1:16 (Figure 1). In this kinetic-focused study, the biogas was delivered at a constant flow rate of 1 L/min using a vacuum pump, ensuring a steady and uniform contact time with the adsorbent media.

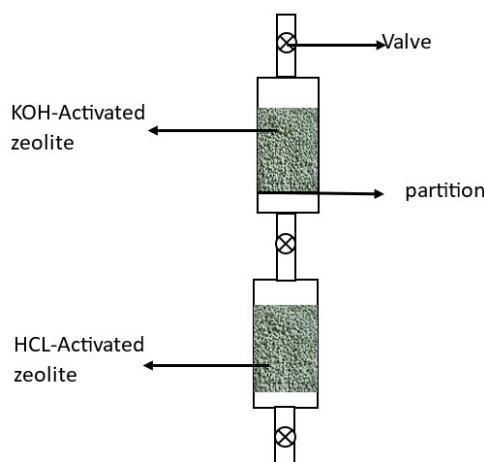


Fig. 1. Two-stage adsorption column

Gas composition, including CH₄, CO₂, and H₂S, was continuously monitored using a portable infrared biogas analyzer (TY-6300P). The device's technical specifications are shown in Table 1. Measurements were taken at 10-minute intervals for a duration of 5 hours to obtain adsorption profiles over time. Two particle traps were installed in the line before the analyzer to prevent interference from particulates or condensates.

Each test was repeated three times for reproducibility, and prior to every new run, the adsorption columns were cleaned thoroughly. The initial gas composition from raw biogas was recorded as 61.54% CH₄, 33.32% CO₂, and 290 ppm H₂S. The breakthrough and saturation curves for CO₂ were analyzed to determine adsorption efficiency and kinetic behavior throughout the purification period.

TABLE I. TECHNICAL PARAMETERS OF THE BIOGAS ANALYZER

Technical parameters	CH ₄	CO ₂	H ₂ S
Measurement indicators	0-100%	0-50%	0-9999 ppm
Resolution	0.01%	0.01%	1 ppm
Measurement accuracy	±2% FS	±2% FS	±3% FS
Repeatability error		≤1% FS	
Stability	Zero drift ≤1%FS/7d		Range drift ≤1%FS/7d
Intake air flow		0.7~1. L/min	
Intake pressure		0~150 kPa	

III. RESULTS AND DISCUSSION

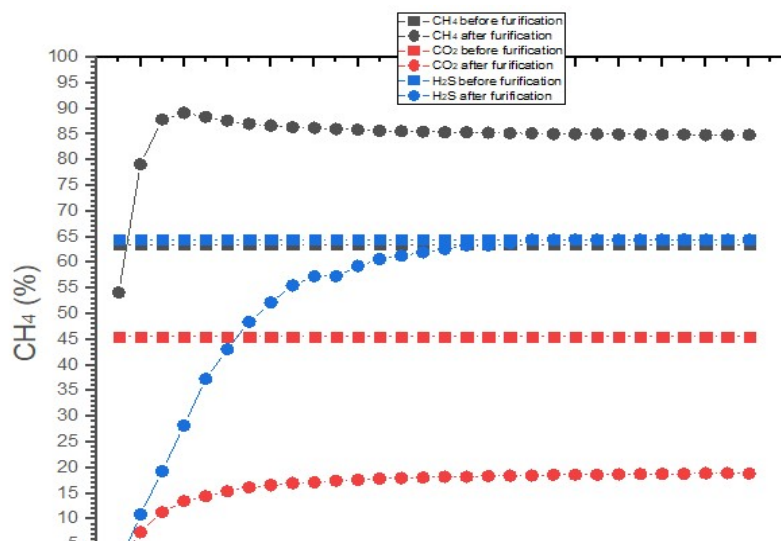


Fig. 2. Concentration profiles of CH₄, CO₂, and H₂S before and after biogas purification using a two-stage system with natural zeolite activated by 20% KOH (stage 1) and 3 M HCl (stage 2).

Figure 2 illustrates the effectiveness of the purification process in enhancing biogas quality by reducing impurities such as CO₂ and H₂S while significantly increasing methane (CH₄) concentration. According to adsorption theory, biogas upgrading is based on the principle of adsorption, which involves the adhesion of gas molecules onto the surface of a solid material. Zeolite, as a natural adsorbent, is characterized by its microporous structure and large surface area, making it highly effective in capturing small gas molecules like CO₂ and H₂S.

Chemical activation using KOH (a strong base) increases the number of hydroxyl groups on the zeolite surface, enhances surface area, and opens up pores to optimize CO₂ adsorption. Conversely, HCl activation (a strong acid) removes metal impurities and improves the structural stability of zeolite, enabling better adsorption of acidic and corrosive molecules such as H₂S.

The graph shows that after purification, CH₄ concentration increased from approximately 60% to around 95%, CO₂ decreased from 40% to about 15%, and H₂S dropped from nearly 400 ppm to close to 0 ppm within the first two minutes. These results outperform previous studies. For example, a previous study reported an increase in CH₄ concentration to only 85% and a CO₂ reduction of approximately 20% using zeolite activated through physical and chemical methods. In another study, H₂S levels could only be reduced to around 50 ppm using H₂SO₄-activated zeolite [10]. In contrast, the current study demonstrates a significantly more effective H₂S removal using zeolite activated with 3 M HCl.

These findings confirm that a dual-stage activation approach—employing both KOH and HCl—delivers superior purification performance compared to single-stage systems. This aligns with the theoretical premise that different activating agents target different impurities: KOH is more effective against CO₂ due to its affinity for weakly acidic gases, while HCl is more suitable for capturing H₂S. Therefore, this two-stage strategy not only improves the energy content of biogas but also minimizes the risks associated with corrosive and non-combustible gases. This makes the process especially valuable for small-scale and household applications, offering a practical and economical method for clean energy production.

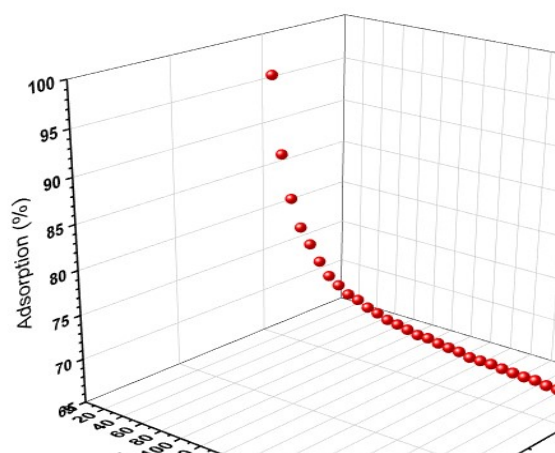


Fig. 3. Three-dimensional representation of CO₂ adsorption efficiency over time during two-stage purification using sequentially activated natural zeolite

Figure 3 reveals that during the initial stage of purification, particularly within the first 60 seconds, CO₂ adsorption efficiency was extremely high, approaching 100%. However, efficiency declined exponentially over time, reaching approximately 70% by the 300th second. This trend reflects the initially abundant availability of active sites on the zeolite surface, which progressively become saturated with CO₂ molecules, leading to decreased adsorption performance.

Theoretically, this phenomenon is explained by adsorption isotherm and kinetic models such as Langmuir and Freundlich, which describe how adsorption occurs on solid surfaces and how it reaches equilibrium depending on surface characteristics and the affinity between adsorbate and adsorbent [11,12]. The zeolites used in this study had been chemically activated using KOH and HCl, both of which significantly enhanced the specific surface area and the number of active pores. KOH activation increases the presence of Lewis base sites, promoting interactions with acidic CO₂ molecules [13]. Meanwhile, HCl activation enhances surface acidity and develops additional micropores.

The two-stage purification system demonstrated high efficacy by allowing CO₂ removal to occur in two chemically distinct environments. The first stage, with KOH-activated zeolite, enhances CO₂ affinity through base–acid interactions, while the second stage, with HCl-activated zeolite, offers extended porosity for additional adsorption. This synergy results in high initial adsorption efficiency, although—as shown in the graph—the performance gradually declines as the adsorbent approaches saturation. This underscores the necessity for periodic regeneration of the adsorbent material to maintain optimal performance.

Compared to earlier studies, which reported a maximum CO₂ adsorption efficiency of only 60–70% when using unactivated natural zeolite, the performance achieved in the present study is substantially higher [14]. Furthermore, other investigations have shown that dual-activation methods are capable of increasing adsorption efficiency to over 90% within a shorter duration, thereby supporting the results obtained in this work [15]. Therefore, the dual-stage biogas purification strategy using chemically activated zeolite is both effective and practical for improving biogas quality. It represents a promising approach for widespread application in renewable energy systems.

IV. CONCLUSION

This study successfully demonstrates that a two-stage biogas purification system using natural zeolite activated with 20% KOH and 3 M HCl significantly enhances biogas quality by increasing methane concentration and reducing contaminant levels. The initial stage utilizing KOH-activated zeolite effectively targets CO₂ due to its basic surface properties, while the subsequent HCl-activated stage enhances further adsorption through increased porosity and acidic site interactions. Kinetic analysis of CO₂ adsorption revealed high efficiency in the early phase of the process, reaching up to 100% within the first minute, followed by a gradual decline due to saturation of active sites. These findings are supported by adsorption theory, particularly Langmuir and

Freundlich models, which explain the behavior of adsorbate-adsorbent interactions over time. Compared to previous single-stage or non-activated systems, the dual-activation strategy provides superior performance, especially in CO₂ and H₂S removal. This approach not only improves the calorific value and safety of biogas but also represents an economically viable and scalable method for rural or small-scale energy systems. Further research is recommended to explore regeneration strategies for prolonged adsorbent usability and optimization under continuous-flow conditions.

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