

Article

Beyond Methane Formation: Product Dilution and the Conditional Relevance of Methane-Selective Extraction in Batch Photocatalytic CO₂ Reduction

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Abstract

Photocatalytic CO₂-to-CH₄ conversion is usually assessed through catalyst activity, selectivity, and methane formation rate, although the practical usefulness of the resulting gas stream also depends on methane recovery from CO₂-rich mixtures. Here, a phenomenological Langmuir–Hinshelwood reactor model was used to evaluate batch gas-phase CO₂ photoreduction under different reactor thicknesses, water-availability conditions, photocatalyst activities, and idealized methane-selective extraction configurations. The model considered competitive adsorption, transient gas-phase balances, finite or buffered water supply, and a lumped selective CH₄ extraction term. Under finite vapor inventory, water depletion limited reaction progress, particularly in thin reactors. Buffered-water operation increased CO₂ conversion and methane formation, while reactor thickness produced a trade-off: thin reactors favored apparent conversion and methane enrichment, whereas thicker reactors provided a larger CO₂ reservoir and higher cumulative methane formation. At the baseline kinetic condition, methane extraction strongly decreased the in-reactor CH₄ fraction but only modestly increased methane formation. When photocatalyst activity was increased, the non-membrane thin reactor reached a product-accumulation-limited regime, and methane-selective extraction became kinetically relevant. These results indicate that methane-selective extraction concepts should be evaluated not only as separation devices, but as conditional reactor-intensification tools whose relevance depends on water availability, reactor geometry, catalyst productivity, and product dilution.

Keywords: photocatalytic CO₂ reduction; CO₂-to-CH₄ conversion; Langmuir–Hinshelwood kinetics; gas-phase photoreactor; product accumulation; water availability; idealized methane-selective extraction; methane recovery



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1. Introduction

1.1. Photocatalytic CO₂-to-CH₄ Conversion: Progress and Persistent Process-Level Limitations

Photocatalytic CO₂ reduction remains an attractive route for solar-to-fuel conversion because it combines carbon utilization with mild operating conditions and, at least in principle, direct storage of solar energy in chemical bonds. Among the possible reduction products, methane is especially appealing because it is a fully reduced C₁ fuel and is already compatible with existing gas-handling infrastructure. At the same time, CH₄ is among the most demanding targets in photocatalytic CO₂ reduction, as its formation requires a complex multielectron pathway and strict control over charge separation, surface adsorption, and intermediate stabilization. Recent reviews continue to identify low

productivity, limited reproducibility, and weak process-level translation as central barriers to technological relevance, even while catalyst design has advanced rapidly [1].

Over the last two years, substantial progress has indeed been made at the catalyst level. Vacancy engineering, heterojunction design, and active-site modulation have delivered markedly improved CH_4 selectivity in several systems. A representative example is the S-vacancy-modulated $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$ heterojunction, reported with CH_4 selectivity near 95.9%, illustrating how targeted electronic and structural control can direct the eight-electron reduction pathway toward methane. More broadly, recent reviews emphasize that current catalyst-development strategies are largely centered on improving CO_2 adsorption and activation, increasing the density and effectiveness of active sites, and promoting selective reaction pathways on the photocatalyst surface [2–4]. Recent studies further illustrate this catalyst-centered progress. Donor–acceptor metal–organic frameworks, unsaturated high-spin metal sites, oxygen-vacancy-engineered S-scheme heterojunctions, two-dimensional bismuth-based heterostructures, and metal-halide/ In_2S_3 S-scheme systems have all been explored to improve light absorption, charge separation, CO_2 activation, proton-coupled electron transfer, and product selectivity in photocatalytic CO_2 conversion [5–9].

However, rapid progress in catalyst architecture has not eliminated a more fundamental question: once methane can be formed selectively at the catalyst surface, under what reactor conditions can that advantage be effectively translated into overall reactor performance? This issue is particularly relevant in gas-phase photocatalytic systems, where reaction occurs only at or near the illuminated catalyst surface, while the surrounding gas phase serves as a reservoir of reactants and products. Under these conditions, improved intrinsic catalytic properties do not automatically lead to proportional gains in methane production at the reactor scale. Their practical impact depends on whether the reactor configuration can provide adequate light distribution, efficient access of reactants to the active surface, and sufficient control over product accumulation within the reaction chamber [10].

1.2. Methane Accumulation as an Overlooked Bottleneck in Batch Photoreactors

A notable feature of the recent photocatalytic CO_2 -reduction literature is that performance discussions are still predominantly catalyst-centered, whereas reactor behavior is often treated as a secondary issue. Yet recent analyses of gas–solid photoreactors stress that reactor configuration is itself a critical determinant of performance. The gas–solid mode is increasingly recognized as attractive because of rapid molecular diffusion, adjustable feed composition, and the possibility of relatively uniform illumination, but the same literature also notes that reported gas–solid photoreactors remain at an early stage of development and that reactor design is still underexplored relative to catalyst synthesis.

This imbalance becomes particularly important in batch systems designed for methane production. In a closed or semi-closed photoreactor, CH_4 is not simply a desired product; as it accumulates, it becomes part of the reaction environment. Within a Langmuir–Hinshelwood framework, increasing methane concentration can modify competitive adsorption and alter the apparent kinetic regime. More generally, the same product that is being targeted may progressively contribute to unfavorable local conditions by competing for surface access, perturbing surface coverage, or becoming susceptible to secondary transformation if it remains in the illuminated reactive zone for long enough. Thus, methane accumulation in batch operation should not be viewed as a passive outcome of successful reaction, but as a potential source of kinetic self-limitation.

This interpretation is also consistent with broader trends in reactor engineering [11]. Recent work on automated and flow-based light-assisted CO_2 reduction systems highlights the importance of narrow channels, high catalyst-surface-area exposure, and improved control of mass and heat transfer [12]. These designs implicitly recognize that, for surface-

limited reactions, large gas volumes are not automatically beneficial. What matters is not merely the amount of gas in the reactor, but how effectively that gas can interact with illuminated active sites before product build-up begins to penalize the reaction environment.

1.3. The Relevance of Methane-Selective Extraction

Membrane-coupled photocatalytic systems offer a natural way to address this bottleneck because they combine reaction and separation in a single framework. Recent reviews on photocatalytic membrane reactors describe the field as increasingly focused on the interplay between membrane properties, reactor configuration, reaction kinetics, and operating conditions, and identify membrane integration as a promising route for intensifying solar-driven chemical processes. At the same time, the existing photocatalytic membrane literature remains dominated by environmental remediation, water treatment, and broad energy applications, while methane-selective extraction during gas-phase photocatalytic CO_2 -to- CH_4 conversion appears to be much less systematically explored.

In the present context, the membrane is not introduced primarily as a downstream purification unit. Rather, it is considered as a reactor-level kinetic-management tool. If methane can be removed *in situ* as it forms, its concentration inside the reaction chamber may remain lower than in a conventional batch reactor. That change could be beneficial in at least three ways: it may reduce product-site competition, delay the onset of product inhibition, and shorten the residence time of CH_4 in the irradiated reactive environment. Even before one invokes explicit reverse or secondary back-conversion pathways, selective methane withdrawal could already reshape the local kinetic landscape simply by keeping the reactor farther from a product-rich state. Under this interpretation, the scientific question is not whether methane can be separated in principle, but under which reactor conditions methane-selective removal actually becomes relevant [13].

It is important to note that most CO_2/CH_4 membrane-separation studies are oriented toward removing CO_2 from methane-containing streams, as occurs in natural-gas purification or biogas upgrading, where the objective is to enrich the methane fraction [14–16]. This conventional configuration is different from the scenario explored in the present work. In most practical CO_2/CH_4 membranes, CO_2 permeation is favored because CO_2 is smaller and more condensable than CH_4 ; therefore, the CH_4 -favoring extraction considered here should not be interpreted as a readily available membrane technology.

In this study, the membrane is treated as an idealized methane-selective product-extraction boundary introduced to test a reactor-level question: if methane could be selectively withdrawn from the photoreactor while CO_2 and H_2O losses were strongly suppressed, under which conditions would such withdrawal become kinetically relevant? Achieving this behavior experimentally would likely require an unconventional separation architecture, such as a membrane–sorbent configuration, an active product-extraction interface, or another mechanism capable of retaining or recycling CO_2 and H_2O while preferentially removing CH_4 . Thus, the purpose of the present model is not to claim the near-term availability of a CH_4 -selective CO_2/CH_4 membrane, but to establish the reactor conditions under which selective methane withdrawal would be worth pursuing.

This reinforces the process-level relevance of the present problem: a gas mixture containing only a few percent of CH_4 in a CO_2 -rich stream cannot be assumed to be directly useful as a fuel without additional separation or upgrading [17,18]. This reactor-level concern is also consistent with the broader development of integrated CO_2 capture and conversion strategies, where the value of the conversion step depends not only on forming a target molecule, but also on managing separation, enrichment, and downstream usability of the resulting stream [19].

1.4. Scope and Working Hypothesis of the Present Study

Motivated by the considerations above, this work examines methane-selective extraction from the standpoint of reactor relevance. A phenomenological kinetic model was developed for batch photocatalytic CO₂ reduction to CH₄ in the presence of water vapor, using a Langmuir–Hinshelwood-type description coupled with transient gas-phase mass balances. The model was not intended to reproduce the performance of a specific photocatalyst, but to compare reactor regimes under internally consistent assumptions. The analysis focuses on three variables that emerged as potentially decisive in preliminary exploration: reactor thickness, water availability, and in situ methane extraction. Two limiting water-availability scenarios are considered, namely a strictly batch case with a finite initial inventory of water vapor and a buffered case in which water concentration is maintained at its saturation value throughout operation. A membrane-assisted configuration is then introduced through a selective methane-removal term, allowing direct comparison with the corresponding non-membrane reactor under otherwise identical conditions.

The working hypothesis is that the usefulness of methane-selective extraction is not universal, but conditional. More specifically, the benefit of a methane-selective membrane should depend on the extent to which methane accumulation is able to perturb the kinetic environment inside the reactor, and this sensitivity should be strongly affected by reactor thickness and water availability. In thick reactors with large gas inventories, methane accumulation may remain relatively diluted and membrane effects may therefore be weak. In thinner reactors, by contrast, a smaller gas volume may allow methane concentration to rise more rapidly, making selective extraction increasingly valuable. On this basis, the central objective of this study is to identify the reactor conditions under which methane-selective extraction begins to produce a measurable benefit, and to define a membrane relevance threshold for batch photocatalytic CO₂-to-CH₄ conversion.

Previous kinetic and reactor-simulation studies have provided important foundations for modeling photocatalytic CO₂ reduction. Langmuir–Hinshelwood-type formulations have been used to describe apparent kinetic behavior and product inhibition, while more general kinetic frameworks have emphasized the importance of reaction conditions, surface coverage, and coupled reduction/oxidation processes. Reactor-scale simulations have also shown that geometry, gas inventory, and transport can strongly affect apparent performance. The novelty of the present work lies in combining these ideas to evaluate a specific reactor-level question: how gas-layer thickness, water availability, photocatalyst activity, product accumulation, and idealized methane-selective extraction jointly determine when methane withdrawal becomes relevant in batch gas-phase CO₂-to-CH₄ photoreduction.

2. Results and Discussion

2.1. Reactor Thickness Under Finite Vapor Inventory

Figure 1 shows the effect of reactor thickness on batch photocatalytic CO₂ reduction under finite vapor-inventory conditions after 48 h of operation. In this case, the reactor contains only the initial amount of water vapor present after saturation, with no additional water supplied during the reaction. Therefore, changing the reactor thickness modifies not only the gas-phase volume, but also the way in which the fixed illuminated catalyst surface interacts with a finite inventory of CO₂ and H₂O.

The first clear trend is that decreasing the gas-layer thickness increases the apparent CO₂ conversion. After 48 h, the 5 mm reactor reaches the highest conversion, 1.42%, followed by the 10 mm reactor with 1.28%, whereas the 50 mm reactor reaches only 0.72% (Table 1). This behavior is consistent with the increase in catalyst-to-gas-volume ratio as the chamber becomes thinner. Since the same catalytic surface acts on a smaller gas inventory, a

given extent of reaction produces a larger change in gas composition. In this sense, thinner reactors amplify the compositional response of the batch system.

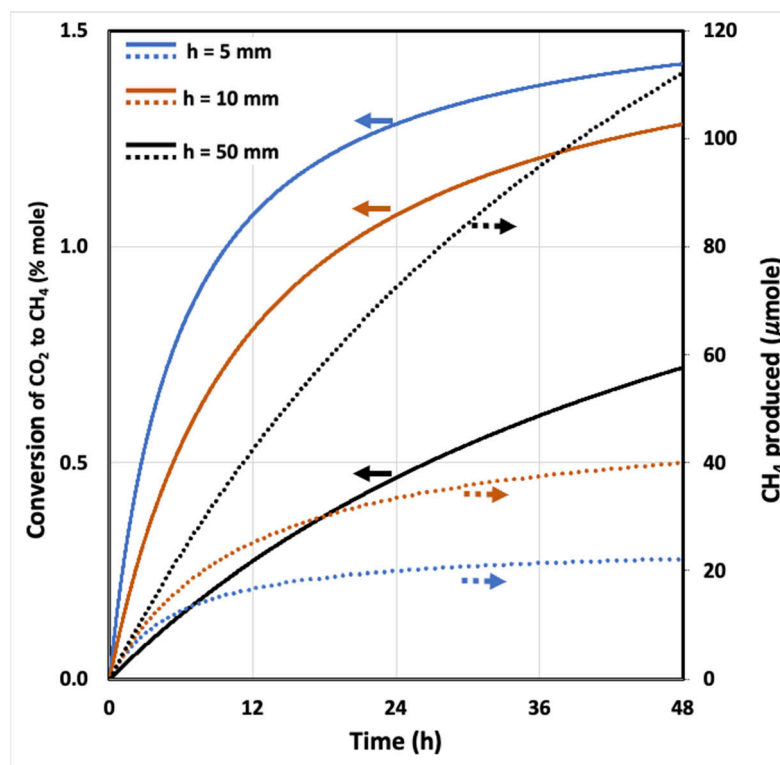


Figure 1. Effect of reactor thickness (5, 10, and 50 mm) on apparent CO₂-to-CH₄ conversion (solid lines, left axis) and total CH₄ produced (dotted lines, right axis) under finite vapor-inventory conditions.

Table 1. Final values obtained after 48 h of operation for both water-availability scenarios, including apparent CO₂ conversion, H₂O consumption in the finite-vapor case, the final molar fractions of CO₂ and CH₄ in the reactor and the amount of CH₄ formed during the reaction time.

H ₂ O Availability (mole/L)	Variable, Starting with 0.001267			Constant (0.001267)		
Photoreactor Height (mm)	5	10	50	5	10	50
Photoreactor Volume (mL)	39.3	78.5	392.7	39.3	78.5	392.7
Final CO ₂ Conversion (%)	1.42	1.28	0.72	10.52	5.85	1.28
Final H ₂ O Consumption (%)	89.0	80.3	45.1	NA	NA	NA
CO ₂ Molar fraction (% mole)	95.5	95.7	96.2	72.0	82.0	93.3
CH ₄ Molar fraction (% mole)	1.4	1.2	0.7	8.5	5.1	1.2
CH ₄ Formed (μ-mole)	22	40	112	164	182	200

NA = Not applicable. Under buffered-water conditions, the water concentration in the gas phase is maintained constant at its saturation value; therefore, H₂O consumption is not defined.

However, the total amount of methane formed follows a different trend. Although the 5 mm reactor gives the highest apparent conversion, the 50 mm reactor produces the largest total methane amount after 48 h. The methane formed increases from 22 μmol in the 5 mm reactor to 40 μmol in the 10 mm reactor and 112 μmol in the 50 mm reactor. This apparent contradiction is a direct consequence of the batch nature of the system. A thicker reactor contains a larger initial inventory of CO₂; therefore, even if the fractional conversion is lower, the absolute number of moles available for reaction is higher. In addition, because

methane formation depends on the CO₂ concentration in the kinetic expression, the larger reactant reservoir in the thicker reactor helps sustain methane production over time.

This result highlights an important distinction: apparent conversion and total methane inventory are not equivalent performance metrics [20]. A thin reactor is more effective at increasing the fraction of CO₂ converted because the gas volume is small. A thick reactor, in contrast, can produce more methane in absolute terms because it contains more reactant. Thus, reactor thickness changes the interpretation of performance depending on whether the objective is to maximize fractional conversion, methane concentration, or total methane amount per batch.

The finite-vapor case also shows that water availability becomes a relevant limitation, especially in the thinner reactors. After 48 h, water-vapor consumption reaches 89.0% in the 5 mm reactor and 80.3% in the 10 mm reactor, compared with 45.1% in the 50 mm reactor (Table 1). This indicates that the geometries that most strongly intensify the reaction also deplete the finite water inventory more rapidly. As a result, the benefit of decreasing reactor thickness is progressively constrained by the limited amount of water vapor initially present in the closed system.

The final gas composition reinforces this interpretation. Even after 48 h, the methane mole fraction remains low under finite vapor-inventory conditions: 1.4% for the 5 mm reactor, 1.2% for the 10 mm reactor, and 0.7% for the 50 mm reactor. Therefore, although decreasing reactor thickness improves apparent conversion, it does not produce a methane-rich gas phase. The product remains highly diluted in CO₂, which is a critical limitation from a process standpoint.

Accordingly, Figure 1 establishes three main points. First, reducing reactor thickness intensifies the response of the batch photoreactor and increases apparent CO₂ conversion. Second, total methane formation does not necessarily follow the same trend, because thicker reactors contain a larger reactant inventory. Third, under finite vapor-inventory conditions, water depletion and methane dilution remain major constraints. Therefore, reactor evaluation should not rely only on apparent conversion, but should also consider methane amount, final product composition, and the practical implications of recovering methane from a highly diluted gas stream.

2.2. Buffered-Water Operation Confirms That Water Availability Is a Regime-Defining Variable

Figure 2 and Table 1 show the corresponding results when water is maintained at its saturation concentration throughout the simulation. Under these buffered-water conditions, the effect of reactor thickness becomes much more informative because water depletion is removed as an immediate limiting factor.

After 48 h, the 5 mm reactor reaches 10.52% CO₂ conversion, while the 10 mm and 50 mm reactors reach 5.85% and 1.28%, respectively. Compared with the finite-vapor case, maintaining water availability increases conversion by factors of approximately 7.4, 4.6, and 1.8 for the 5, 10, and 50 mm reactors, respectively. This confirms that finite water inventory was not a secondary detail but a regime-defining constraint, especially in thin reactors.

The same conclusion is obtained from the methane mole fraction. Under buffered-water conditions, the final CH₄ content reaches 8.5% in the 5 mm reactor and 5.1% in the 10 mm reactor, compared with only 1.2% in the 50 mm reactor. These values are much higher than those obtained under finite-vapor operation, showing that water replenishment allows the thin reactors to take better advantage of their higher catalyst-to-gas-volume ratio.

Nevertheless, the distinction between conversion and total methane formation remains. The 5 mm reactor gives the highest methane concentration and the highest apparent conversion, but the 50 mm reactor still produces the largest total methane amount, 200 μmol after 48 h, compared with 182 μmol for the 10 mm reactor and 164 μmol for the 5 mm

reactor. Again, this reflects the larger reactant inventory in the thicker reactor. Therefore, thin reactors are preferable when methane enrichment is the priority, whereas thicker reactors can be favorable when the metric is total methane produced per batch.

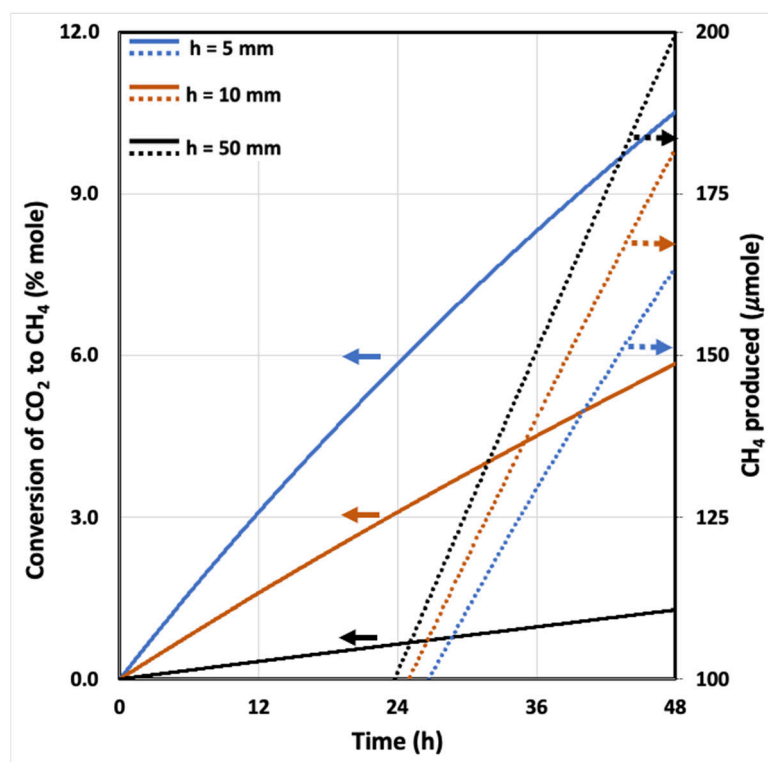


Figure 2. Effect of reactor thickness (5, 10, and 50 mm) on apparent CO₂-to-CH₄ conversion (solid lines, left axis) and total CH₄ produced (dotted lines, right axis) under buffered-water conditions.

Despite the significant improvement obtained by buffering water, the product stream is still far from being methane-rich. Even in the most favorable case, the 5 mm reactor contains 72.0 mol% CO₂ and only 8.5 mol% CH₄ after 48 h. Thus, water buffering improves both conversion and methane concentration, but it does not eliminate the process-level challenge of product dilution. This point is central for evaluating the potential role of methane-selective extraction.

2.3. Baseline Membrane-Assisted Operation: Extraction Is Effective, but Kinetic Enhancement Is Limited

The idealized membrane-assisted simulations were introduced to determine whether selective methane removal could improve reactor performance by lowering methane accumulation inside the reaction chamber. This is not a trivial point because, in a membrane-assisted system, the methane remaining inside the reactor is no longer equivalent to the methane formed by reaction. A low methane fraction in the chamber may simply indicate efficient extraction rather than poor methane productivity.

At the baseline kinetic condition, $k_1 = 0.01$, the membrane strongly reduces methane accumulation inside the reactor but produces only a modest increase in total methane formation. In the 5 mm reactor under buffered-water conditions, the final CH₄ mole fraction decreases from 8.5% without membrane to 0.6% with membrane, while the amount of methane formed increases from 164 to 179 μmol (Table 2). The corresponding apparent CO₂ conversion increases only from 10.5% to 11.5%. Thus, under the baseline activity regime, the membrane is clearly effective as a methane-withdrawal element, but its impact on the reaction rate remains limited.

Table 2. Final values obtained after 48 h under buffered-water conditions (water availability constant) for 5 and 50 mm reactors, with and without an idealized CH₄-selective extraction boundary, under three photocatalytic activity conditions ($k_1 = 0.01, 0.05$ and 0.10). The table includes apparent CO₂ conversion, final CO₂ and CH₄ mole fractions in the reactor and cumulative CH₄ formed.

Photoreactor Height (mm)	5						50					
Separation CH ₄ /CO ₂ Membrane	Without Membrane			With Membrane			Without Membrane			With Membrane		
Constant k_1	0.01	0.05	0.10	0.01	0.05	0.10	0.01	0.05	0.10	0.01	0.05	0.10
Final CO ₂ Conversion (%)	10.5	24.9	26.5	11.5	36.3	49.4	1.3	5.8	10.5	1.3	6.2	11.5
CO ₂ Molar fraction (% mole)	72.0	49.0	47.1	73.3	40.0	27.9	93.3	81.9	72.0	93.3	83.0	73.3
CH ₄ Molar fraction (% mole)	8.5	16.3	17.0	0.6	1.0	0.9	1.2	5.1	8.5	0.1	0.4	0.6
CH ₄ formed (μ-mole)	164	388	412	179	564	768	200	910	1637	208	970	1792

The same conclusion is reinforced by the 50 mm reactor at $k_1 = 0.01$. In this case, the methane mole fraction decreases from 1.2% without membrane to 0.1% with membrane, but the amount of methane formed increases only from 200 to 208 μmol. The conversion remains essentially unchanged at approximately 1.3%. This shows that, when methane accumulation is modest, either because the catalyst productivity is low or because the reactor volume is large enough to dilute the product, methane-selective extraction does not substantially alter the reactor trajectory.

This result refines the role of the membrane. At the reference activity level, product accumulation is not yet the dominant kinetic bottleneck. The membrane can remove methane from the reaction chamber, but the reactor does not respond with a proportional increase in methane formation. In other words, methane-selective extraction is necessary to control product inventory, but it becomes kinetically meaningful only if methane accumulation is sufficiently high to perturb the Langmuir–Hinshelwood surface environment.

2.4. Intensified Catalytic Activity Reveals a Membrane Relevance Threshold in Thin Reactors

To test whether the previous conclusion remains valid under more productive catalytic conditions, additional simulations were performed under buffered-water operation by increasing the methane-formation kinetic constant, k_1 , while keeping the remaining model parameters unchanged. This analysis is particularly useful because it simulates the effect of a more active photocatalyst without changing reactor geometry, water availability, or membrane properties.

Figure 3 shows the effect of increasing k_1 in the 5 mm reactor without methane-selective extraction. As expected, increasing k_1 accelerates CO₂ conversion and methane formation. However, the response is clearly non-proportional. At 48 h, increasing k_1 from 0.01 to 0.05 raises the apparent CO₂ conversion from 10.5% to 24.9%, and the amount of methane formed from 164 to 388 μmol (Table 2). In contrast, a further increase in k_1 from 0.05 to 0.10 produces only a small additional improvement, reaching 26.5% conversion and 412 μmol of methane. Thus, once the intrinsic methane-formation rate becomes sufficiently high, the reactor no longer responds linearly to additional catalyst activity.

This behavior reveals the onset of a product-accumulation-limited regime. In the absence of methane extraction, the reactor initially benefits from the higher kinetic constant, but the increasing concentration of products progressively modifies the gas-phase environment and penalizes the apparent reaction rate through the Langmuir–Hinshelwood adsorption term. Therefore, the plateau-like behavior observed at high k_1 should not be interpreted as a limitation of the kinetic constant itself, but as a reactor-level limitation associated with the accumulation of reaction products in a small gas inventory.

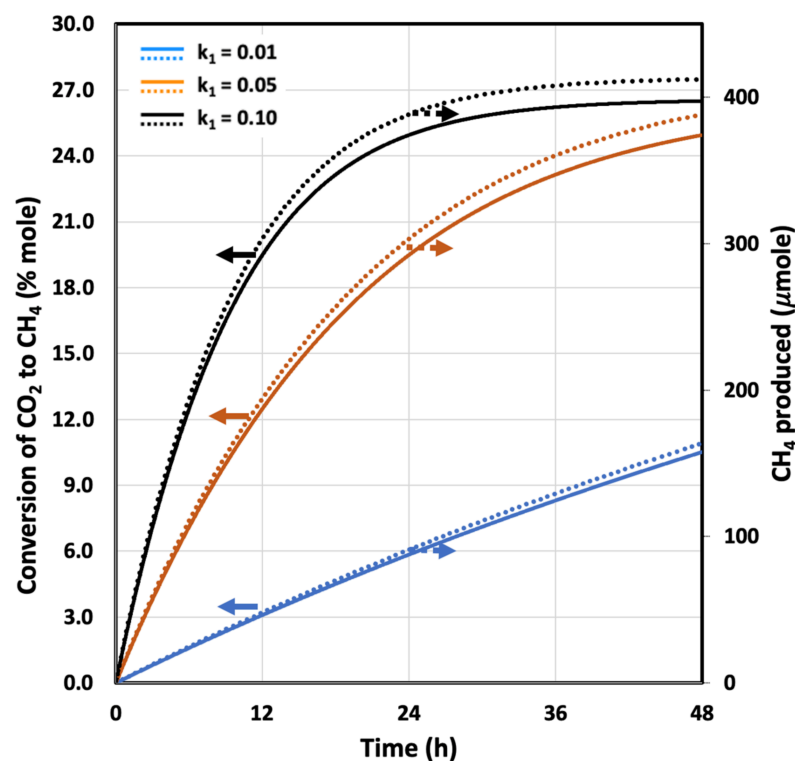


Figure 3. Effect of increasing photocatalyst activity ($k_1 = 0.01, 0.05$ and 0.10) on apparent CO_2 -to- CH_4 conversion (solid lines, left axis) and total CH_4 produced (dotted lines, right axis) under buffered-water conditions, for a 5 mm-height reactor, and without an idealized CH_4 -selective extraction boundary.

The role of the membrane becomes much clearer when Figure 4 is compared with Figure 3. In the 5 mm reactor, methane-selective extraction has only a limited effect at $k_1 = 0.01$, as discussed above. However, the effect becomes much stronger as catalyst activity increases. At $k_1 = 0.05$, the membrane increases conversion from 24.9% to 36.3% and methane formation from 388 to 564 μmol . At $k_1 = 0.10$, the effect is even more pronounced: conversion increases from 26.5% without membrane to 49.4% with membrane, while methane formation increases from 412 to 768 μmol .

The interpretation of this enhancement requires caution because CH_4 is not the only product accumulating in the reactor. O_2 is formed at twice the CH_4 rate and remains in the gas phase because no O_2 -extraction term was included. Consequently, the membrane-assisted improvement should not be interpreted as complete suppression of product inhibition. In the reference simulations, ($K_{\text{CH}_4} = K_{\text{O}_2}$), so O_2 makes a substantial contribution to the adsorption denominator, particularly at high conversion. Selective CH_4 withdrawal therefore mitigates only one component of the product-rich environment. Its effect arises from two coupled contributions: first, reducing P_{CH_4} decreases the $K_{\text{CH}_4} P_{\text{CH}_4}$ term in the adsorption denominator; second, and more importantly under high-productivity conditions, lowering P_{CH_4} suppresses the product-dependent reverse term, which contains the factor $P_{\text{CH}_4} (P_{\text{O}_2})^2$. Thus, the near-doubling of methane formation observed in the 5 mm reactor at $k_1 = 0.10$ does not imply that O_2 accumulation is negligible. Rather, it indicates that removing CH_4 from a coupled CH_4/O_2 product-accumulation regime can still shift the net reaction trajectory, even while O_2 remains an important limiting product.

These results demonstrate that the membrane is not intrinsically irrelevant. Rather, its relevance is conditional on the productivity of the reactor. Under the baseline kinetic regime, methane is formed too slowly for its accumulation to strongly inhibit the reaction. Under intensified catalytic operation, however, methane accumulation becomes sufficiently

important to perturb the reaction environment. In that regime, selective methane extraction no longer acts only as a separation step; it becomes a kinetic-management strategy that allows the reaction to continue advancing beyond the apparent plateau observed in the non-membrane reactor.

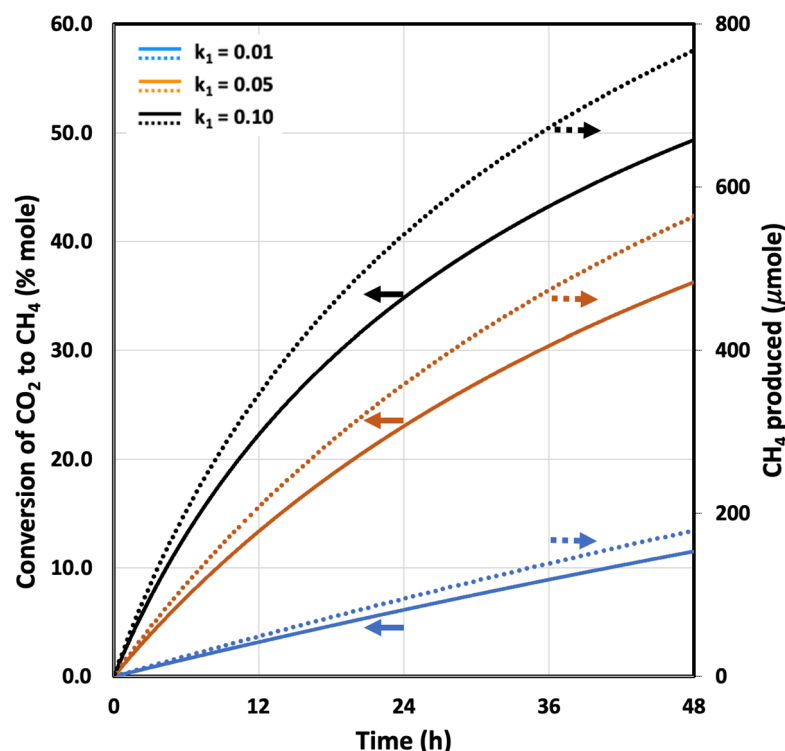


Figure 4. Effect of increasing photocatalyst activity ($k_1 = 0.01, 0.05$ and 0.10) on apparent CO_2 -to- CH_4 conversion (solid lines, left axis) and total CH_4 produced (dotted lines, right axis) under buffered-water conditions, for a 5 mm-height reactor, and with an idealized CH_4 -selective extraction boundary.

An additional point must be emphasized. In membrane-assisted operation, the methane mole fraction remaining inside the reactor is not a direct measure of methane formation. For example, at $k_1 = 0.10$ in the 5 mm reactor, the final methane mole fraction in the chamber decreases from 17.0% without membrane to only 0.9% with membrane, even though the total amount of methane formed increases from 412 to 768 μmol . This apparent contradiction confirms that, when extraction is active, reactor methane concentration and methane productivity must be interpreted separately. The low CH_4 fraction inside the reactor is not evidence of poor methane formation; it is evidence that methane is being continuously removed from the reaction volume.

2.5. Large Gas Inventories Shift the Dominant Benefit from Conversion to Methane Amount

The analysis of the 50 mm reactor adds another layer to the interpretation. Figure 5 shows the effect of increasing k_1 in the 50 mm reactor with methane-selective extraction, while Table 2 allows direct comparison with the corresponding non-membrane case. The result is remarkable because the 50 mm reactor produces much more methane in absolute terms than the 5 mm reactor, even though its apparent conversion remains much lower.

At $k_1 = 0.10$, the 5 mm reactor with membrane reaches 49.4% CO_2 conversion and forms 768 μmol of CH_4 . Under the same kinetic and membrane-assisted conditions, the 50 mm reactor reaches only 11.5% conversion, but forms 1792 μmol of CH_4 . This difference is not caused primarily by a stronger membrane effect in the thicker reactor. It is mainly a consequence of the much larger CO_2 inventory available in the 50 mm gas chamber.

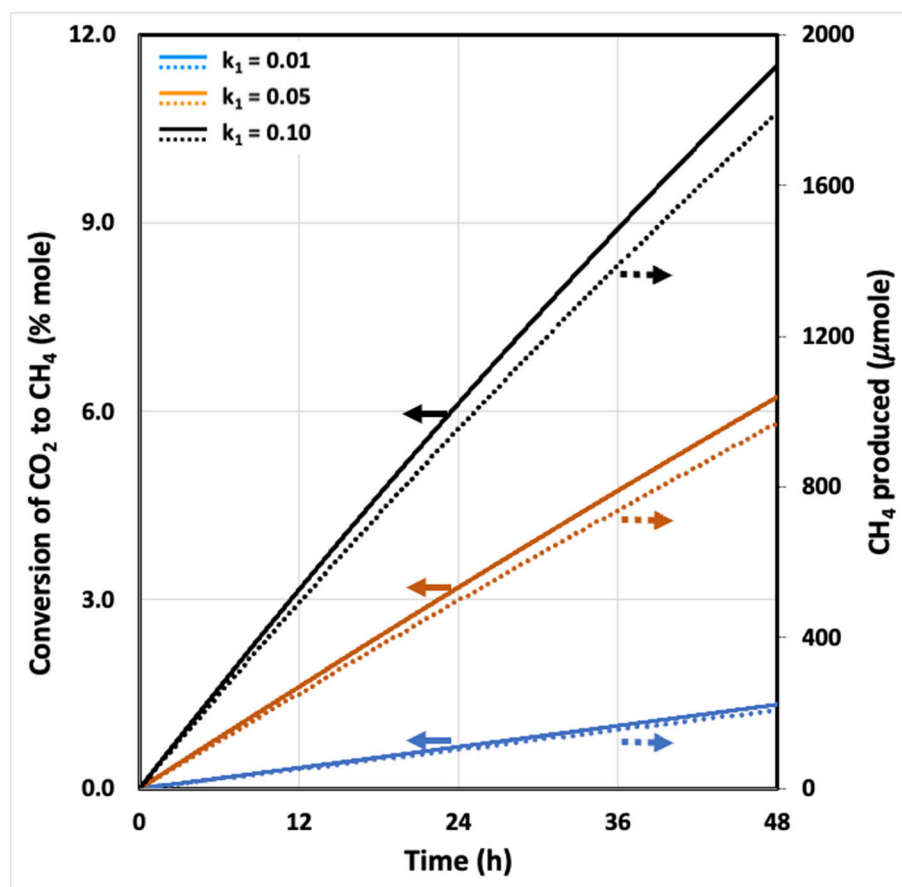


Figure 5. Effect of increasing photocatalyst activity ($k_1 = 0.01$, 0.05 and 0.10) on apparent CO_2 -to- CH_4 conversion (solid lines, left axis) and total CH_4 produced (dotted lines, right axis) under buffered-water conditions, for a 50 mm-height reactor, and with an idealized CH_4 -selective extraction boundary.

This conclusion becomes clear when the 50 mm reactor is compared with and without membrane. At $k_1 = 0.10$, methane formation increases from $1637 \mu\text{mol}$ without membrane to $1792 \mu\text{mol}$ with membrane. This corresponds to a moderate gain, while the final CH_4 mole fraction decreases from 8.5% to 0.6% . The same pattern is observed at $k_1 = 0.05$, where methane formation increases from 910 to $970 \mu\text{mol}$, and the CH_4 mole fraction decreases from 5.1% to 0.4% . Therefore, the membrane is very effective at lowering methane concentration inside the chamber, but its kinetic impact in the 50 mm reactor is modest.

This behavior contrasts markedly with the 5 mm reactor. In the thin reactor at $k_1 = 0.10$, the membrane nearly doubles the total methane formed, from 412 to $768 \mu\text{mol}$. In the 50 mm reactor, the relative gain is much smaller because the larger gas volume already dilutes the methane formed. Product accumulation is therefore less severe, and the kinetic need for methane extraction is reduced. Thus, the larger gas inventory partially performs the same stabilizing role that the membrane provides in the thin reactor: it buffers compositional changes by dilution.

The 50 mm reactor therefore reveals the dual role of reactor thickness. A thinner reactor intensifies the compositional response of the gas phase and reaches higher apparent conversion, but it is more vulnerable to product accumulation when catalytic activity is high. A thicker reactor gives lower apparent conversion, but it provides a larger CO_2 reservoir and dilutes accumulated products. Under buffered-water and high-activity conditions, this larger reservoir can sustain much higher methane production per batch.

Consequently, the optimal reactor thickness depends strongly on the performance criterion being considered. If the objective is to maximize apparent conversion or methane concentration inside the reactor, thin reactors are favored. If the objective is to maximize the total amount of methane formed per batch, a larger gas inventory can be advantageous, especially when water is not limiting. The membrane adds value by controlling methane accumulation, but in thick reactors its role is more clearly associated with product withdrawal than with strong kinetic intensification.

2.6. Implications for Membrane Relevance and Reactor Evaluation

Taken together, Figures 1–5 and Tables 1 and 2 refine the condition at which a membrane becomes relevant. Methane-selective extraction does not provide a universal benefit under all operating conditions. Its effect is weak when catalyst activity is low and methane accumulation is modest. It becomes important when the reactor is sufficiently productive for methane accumulation to perturb the kinetic environment, especially in thin reactors where the gas inventory is small and product mole fractions rise rapidly.

Water availability is the first necessary condition for this threshold to appear. Under finite vapor-inventory conditions, the system is rapidly constrained by water depletion, and membrane extraction cannot compensate for the lack of a reactant. Once water is buffered, the reactor can enter a more productive regime, making product accumulation and methane removal more relevant.

Catalyst activity is the second condition. At the reference k_1 value, methane formation is too slow for methane accumulation to dominate the reaction environment. When k_1 is increased, the non-membrane 5 mm reactor shows clear signs of self-limitation, and the membrane becomes capable of substantially increasing both conversion and cumulative methane formation.

Reactor thickness is the third condition. In thin reactors, the membrane can have a strong kinetic effect because methane accumulation is concentrated in a small gas volume. In thick reactors, the larger CO_2 inventory favors total methane production, but product accumulation is naturally diluted; therefore, the additional kinetic benefit of methane extraction is smaller.

Overall, the results show that methane-selective extraction should not be evaluated only as a separation concept. Its relevance depends on the coupled behavior of catalyst activity, water availability, reactor volume, and product accumulation. For low-activity systems, improving water availability and catalyst productivity is more important than integrating a membrane. For high-activity thin reactors, methane-selective extraction can become a decisive kinetic-management tool. For larger-volume reactors, the membrane remains useful for product withdrawal, but the dominant advantage comes from the larger CO_2 reservoir rather than from strong mitigation of methane inhibition.

3. Model Development

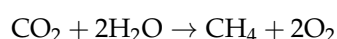
3.1. General Modeling Approach

A phenomenological reactor-scale model was developed to evaluate methane production during batch photocatalytic CO_2 reduction in the presence of water vapor, and to determine under which conditions selective methane extraction becomes relevant. The model was intentionally formulated at an intermediate level of description. It was not intended to provide a fully calibrated predictive description of a specific photocatalyst, but rather to retain the main physicochemical features required to interpret reactor behavior—competitive adsorption, finite gas inventory, water availability, product accumulation, and selective product removal. Accordingly, the model should be interpreted as a scenario-based reactor analysis. Absolute values of conversion and methane formation depend on the selected ki-

netic, adsorption, and extraction parameters; therefore, the emphasis of this work is placed on relative trends and regime transitions, including water-limited operation, gas-inventory, product accumulation, and selective methane withdrawal.

The reaction system was represented as a cylindrical gas-phase batch photoreactor containing a fixed mass of photocatalyst deposited as a thin layer on the bottom surface. Under this configuration, the reaction was assumed to occur only at or near the illuminated catalyst surface, while the bulk gas phase acted as the source of reactants and the sink of products. The reactor was treated as a well-mixed control volume, so that all gas-phase species were described by spatially averaged concentrations. This assumption does not resolve diffusion gradients or dead-volume effects explicitly, but it provides a tractable framework for identifying the reactor conditions under which product accumulation begins to influence performance in a measurable way.

The principal reaction considered was the overall photocatalytic methanation pathway:



which was used as the main source term for methane production. Because the present work focuses on the emergence of membrane relevance rather than on full mechanistic reconstruction, the reaction was represented through an effective Langmuir–Hinshelwood-type net rate. This net rate includes a forward methane-forming contribution and a product-dependent reverse contribution, allowing the model to capture the effect of CH_4/O_2 accumulation on the apparent reactor trajectory without attempting to resolve all elementary photocatalytic steps. Previous kinetic studies on photocatalytic CO_2 reduction and coupled photocatalytic reduction/oxidation systems have shown that L–H formulations are suitable for capturing product inhibition and the progressive emergence of reverse pathways as products accumulate [21].

Because the present work focuses on the emergence of methane-extraction relevance rather than on full mechanistic reconstruction, the reaction was represented through an effective Langmuir–Hinshelwood-type net rate. This net rate includes a forward methane-forming contribution and a product-dependent reverse contribution, allowing the model to capture the effect of CH_4/O_2 accumulation on the apparent reactor trajectory without attempting to resolve all elementary photocatalytic steps.

3.2. Kinetic Formulation

Methane formation was described using a phenomenological Langmuir–Hinshelwood expression, selected to account for the fact that the reaction takes place at the catalyst surface and that the net rate is influenced by competitive adsorption of gas-phase species. Within this framework, carbon dioxide, water vapor, methane, and oxygen were assumed to compete for a common population of active surface sites. The adsorption denominator was written as

$$D = 1 + K_{\text{CO}_2}P_{\text{CO}_2} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}} + K_{\text{CH}_4}P_{\text{CH}_4} + K_{\text{O}_2}P_{\text{O}_2}$$

where K_i is the apparent adsorption constant of species i , and P_i is its partial pressure.

The net methane-formation rate was described as the difference between an effective forward methane-forming term and an effective reverse/product-dependent term:

$$r_1 = r_{1,\text{dir}} - r_{1,\text{rev}}$$

with

$$r_{1,\text{dir}} = \frac{k_1(K_{\text{CO}_2}P_{\text{CO}_2})(K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}})^2}{D^3}$$

and

$$r_{1,rev} = \frac{(k_1/K_{eq,1})(K_{CH_4}P_{CH_4})(K_{O_2}P_{O_2})^2}{D^3}$$

where k_1 is the apparent kinetic constant for the forward methane-forming route and $K_{eq,1}$ is an effective equilibrium like parameter used to scale the product-dependent reverse contribution. This formulation is not intended to represent a complete elementary mechanism. Rather, it provides a compact phenomenological description that allows the model to capture two effects that are relevant in batch operation: the decrease in apparent forward rate caused by competitive adsorption of accumulated products, and the increasing contribution of a product-dependent reverse term as CH_4 and O_2 accumulate in the gas phase.

The role of oxygen must be considered explicitly because, according to the overall stoichiometry, O_2 is produced at twice the CH_4 formation rate. Therefore, product accumulation in this model is not attributed exclusively to methane. Both CH_4 and O_2 contribute to the competitive adsorption denominator through the terms $K_{CH_4}P_{CH_4}$ and $K_{O_2}P_{O_2}$ respectively. In the reference parameter set used here, K_{CH_4} and K_{O_2} were assigned the same value; therefore, the model does not assume a hidden ordering in which methane adsorption is intrinsically much stronger than oxygen adsorption. Under these assumptions, selective CH_4 withdrawal can only partially relieve product accumulation in the adsorption denominator because O_2 remains in the reactor. However, lowering P_{CH_4} also decreases the product-dependent reverse contribution, $r_{1,rev}$ which is proportional to $P_{CH_4}(P_{O_2})^2$. Thus, the effect of CH_4 extraction should be interpreted as a partial mitigation of a coupled CH_4/O_2 product-accumulation regime, rather than as the complete removal of product inhibition.

The present formulation deliberately focuses on the methane-forming route and does not attempt to describe the full product-distribution network of photocatalytic CO_2 reduction. In real systems, CO , $HCOOH$, CH_3OH , and other intermediates or products may form depending on the photocatalyst, reaction medium, light intensity, and operating conditions. Including these species would require additional adsorption constants, kinetic pathways, selectivity relationships, and possibly phase-partitioning assumptions. Because the objective of this work is to evaluate the reactor-level consequences of CH_4 accumulation and idealized CH_4 withdrawal, these additional routes were not included in the reference model. Therefore, the model should be interpreted as a methane-focused phenomenological framework rather than as a complete mechanistic description of photocatalytic CO_2 reduction.

Because the model was not calibrated against a specific experimental dataset, the numerical results should be interpreted as scenario-based comparative simulations rather than as absolute predictions for a particular photocatalyst. The purpose of varying k_1 , reactor thickness, water availability, and membrane extraction was to identify qualitative regimes and relative trends: water-limited operation, product-accumulation effects, and the conditions under which methane-selective extraction becomes kinetically relevant. This phenomenological interpretation was maintained throughout the analysis.

In the baseline simulations, k_1 was set to 0.01 in the units of the adopted rate expression. This value was used as the reference kinetic condition to represent a low-to-moderate activity photocatalytic regime, consistent with the limited conversions typically encountered in gas-phase batch CO_2 photoreduction systems. Additional values of $k_1 = 0.05$ and 0.10 were then explored as photocatalytic activity-intensified scenarios, corresponding to fivefold and tenfold increases in the apparent methane-formation constant relative to the baseline case. These simulations were not intended to modify the adsorption properties of the photocatalyst or to introduce a different reaction mechanism. Instead, they were used to isolate the effect of increasing intrinsic methane-formation activity while keeping the

adsorption constants, reactor geometry, water-availability condition, and membrane parameters unchanged. This approach makes it possible to evaluate whether methane-selective extraction remains marginal under low-productivity conditions or becomes relevant once photocatalyst activity is high enough for methane accumulation to perturb the kinetic environment of the reactor.

The cubic form of the denominator was retained as a practical approximation to represent multispecies surface occupation in a reaction involving several adsorbed participants. In the present study, this formulation is not intended as a full elementary mechanism, but rather as an effective kinetic law capable of capturing product accumulation effects through the dependence of the rate on methane and oxygen partial pressures in the adsorption term.

This point is central to the interpretation of the model. Product accumulation influences the reactor through two coupled effects: competitive adsorption in the Langmuir–Hinshelwood denominator and the product-dependent reverse contribution. Thus, methane-selective extraction can be beneficial not because it eliminates all product inhibition, but because it lowers P_{CH_4} , partially mitigates the product-rich kinetic environment, and reduces the reverse contribution associated with accumulated CH_4 and O_2 . This representation is consistent with prior photocatalytic kinetic studies where coupled reduction and oxidation terms were required to reproduce experimentally observed behavior [22–24].

3.3. Batch Reactor Mass Balances

Because the photoreactor was operated in batch mode, species evolution was described by transient gas-phase balances written in terms of concentration. The gas phase was treated as ideal, so that partial pressures were obtained from

$$P_i = C_i RT$$

where C_i is the gas-phase concentration of species i , R is the gas constant, and T is the absolute temperature.

The transient balances for the main reaction system were written as

$$\frac{dC_{CO_2}}{dt} = -\alpha r_1$$

$$\frac{dC_{H_2O}}{dt} = -2\alpha r_1$$

$$\frac{dC_{CH_4}}{dt} = \alpha r_1$$

$$\frac{dC_{O_2}}{dt} = 2\alpha r_1$$

where

$$\alpha = \frac{W_{eff}}{V}$$

V is the reactor gas volume and W_{eff} is the effective catalyst mass participating in the illuminated reaction zone.

The use of W_{eff} instead of the nominal catalyst mass is important because the photocatalyst was assumed to be deposited on the bottom of the reactor rather than homogeneously suspended throughout the gas volume. Under such conditions, not all of the nominal catalyst mass must necessarily contribute equally to the illuminated reaction zone. To account for this, an activity factor f_{act} was introduced such that

$$W_{eff} = f_{act} W$$

where W is the nominal catalyst mass and $0 < f_{act} \leq 1$. This treatment allows the model to account, in a compact way, for incomplete illumination, non-uniform catalyst distribution, or imperfect utilization of the deposited photocatalyst without changing the formal structure of the governing equations.

3.4. Reactor Geometry and Thickness Variation

The reactor was represented as a cylindrical batch photoreactor of fixed diameter, with variable height used to explore the effect of reactor thickness on system behavior. The photocatalyst was assumed to form a thin layer on the bottom surface, so that the illuminated catalytic area was taken as the cross-sectional area of the cylinder,

$$A_{ill} = \pi r^2$$

where r is the reactor radius.

The reactor gas volume was expressed as

$$V = \pi r^2 h$$

where h is the gas-layer thickness or reactor height. In this way, decreasing h reduces the gas inventory while preserving the illuminated area, thereby increasing the catalyst-to-gas-volume ratio and amplifying the sensitivity of the reactor composition to surface reaction. This variable was treated as one of the primary design parameters of the study.

The rationale for exploring thickness is straightforward. In a gas–solid photocatalytic reactor, the reaction is confined to the illuminated catalyst surface, while the gas volume serves as an inventory of reactants and products. Therefore, changing the gas-layer thickness alters not only the total number of moles present in the reactor, but also the rate at which product accumulation and reactant depletion perturb the local kinetic environment. In this work, reactor thickness was used as a practical descriptor of that coupling.

3.5. Initial Conditions and Water-Availability Scenarios

The influence of reaction medium and water availability has been repeatedly identified as a critical factor in photocatalytic CO₂ reduction [23,25]. This is particularly relevant in gas-phase systems, where water is supplied as vapor and may either be limited to the initial gas inventory or replenished during operation. On this basis, two limiting water-availability scenarios were considered. Experimentally, the reactor is charged by flowing CO₂ through a water saturator and then through the reaction chamber until the outlet composition becomes constant and residual air is displaced. Under these conditions, the initial gas composition corresponds to CO₂ saturated with water vapor at the operating temperature. The second scenario represents permanent water provision.

In Case I (finite vapor inventory), the reactor is treated as a strictly closed batch system. The initial concentration of water vapor is determined by saturation at the operating temperature, but no additional water is supplied during the reaction. In this case, water vapor is progressively consumed and may become limiting as the reaction proceeds.

In Case II (buffered water), the water concentration is maintained at its saturation value throughout the simulation. This case represents the presence of an additional water reservoir capable of replenishing vapor during operation, such as liquid water elsewhere in the system, adsorbed moisture on the catalyst, or continuous gas–surface equilibration. In a practical way for experimental implementation, this is equivalent to having a water-

permeable membrane as a support for the photocatalyst, and underneath a reservoir of liquid water. Under this condition, the water balance is replaced by the algebraic constraint

$$C_{H_2O} = C_{H_2O,sat}$$

which allows the model to separate the effect of finite gas-phase water inventory from the intrinsic effect of methane accumulation and methane removal.

These two cases establish lower and upper bounds for water availability and proved particularly useful in identifying whether the reactor is primarily controlled by gas-phase water limitation or by methane accumulation effects.

3.6. Membrane-Assisted Methane Extraction

To evaluate the possible benefit of in situ methane withdrawal, an idealized methane-selective extraction boundary was introduced. This boundary was assigned to the lateral wall of the cylindrical reactor and was formulated to favor methane removal while strongly suppressing CO_2 , O_2 and H_2O losses. The term “membrane” is therefore used in a phenomenological sense in this model. It represents a hypothetical product-extraction function rather than the demonstrated performance of a specific membrane material.

This distinction is important because conventional CO_2/CH_4 membrane separations typically favor CO_2 permeation and are designed to remove CO_2 from methane-rich streams. The configuration considered here is the opposite limiting case: methane is the target product formed at low concentration inside a CO_2 -rich photoreactor, and the model asks what would happen if methane could be preferentially withdrawn from that environment. The assumed selectivities should therefore be interpreted as idealized parameters used to isolate the effect of selective CH_4 withdrawal, not as a claim of currently available membrane performance.

The membrane area was taken as the lateral area of the cylindrical reactor,

$$A_m = \pi Dh$$

where D is the reactor diameter and h is the reactor height. Gas transport through the membrane was described using a linear permeation law driven by the transmembrane partial-pressure difference. Under the simplifying assumption of low permeate-side partial pressure, the extraction term for species i was written in lumped form as

$$\left(\frac{dC_i}{dt} \right)_{mem} = -\beta_i C_i$$

where β_i is an effective extraction coefficient with units of s^{-1} . This parameter combines membrane permeance, membrane area-to-volume ratio, temperature, and the assumed permeate-side driving force into a single global term.

Since the membrane was specifically intended to favor methane removal, the methane extraction coefficient β_{CH_4} was used as the reference parameter, while the extraction coefficients of the other species were related to it through selectivity ratios,

$$\beta_{CO_2} = \frac{\beta_{CH_4}}{S_{CH_4/CO_2}}$$

$$\beta_{H_2O} = \frac{\beta_{CH_4}}{S_{CH_4/H_2O}}$$

where S_{CH_4/CO_2} and S_{CH_4/H_2O} are the methane-over- CO_2 and methane-over-water selectivity, respectively.

For the membrane-assisted simulations, β_{CH_4} was set to $1.0 \times 10^{-4} \text{ s}^{-1}$. This value was selected as a representative extraction intensity for sensitivity analysis rather than as the optimized performance of a specific membrane material. The corresponding characteristic extraction time is $1/\beta_{CH_4} = 1.0 \times 10^4 \text{ s}$, approximately 2.8 h, which is short relative to the 48 h batch reaction time but not so short as to impose instantaneous methane removal. Therefore, the selected value allows methane withdrawal to compete with methane formation while still preserving the dynamic coupling between reaction and accumulation inside the reactor. The same β_{CH_4} value was used for all reactor heights in order to isolate the effects of gas inventory, water availability, and photocatalytic activity. Since the cylindrical diameter was kept constant, the lateral membrane-area-to-volume ratio remains constant for the geometries considered, making this comparison internally consistent. The selectivity ratios S_{CH_4/CO_2} and S_{CH_4/H_2O} were assigned idealized values to represent a limiting case in which CH_4 withdrawal is much faster than CO_2 or H_2O loss. This choice was made to probe the specific effect of selective product removal on reactor behavior. The selected values should not be interpreted as material-performance targets already achieved by conventional CO_2/CH_4 membranes. Instead, they define a hypothetical extraction boundary that allows the kinetic and compositional consequences of methane removal to be isolated from non-selective gas depletion.

With membrane extraction, the mass balances become

$$\begin{aligned}\frac{dC_{CO_2}}{dt} &= -\alpha r_1 - \beta_{CO_2} C_{CO_2} \\ \frac{dC_{H_2O}}{dt} &= -2\alpha r_1 - \beta_{H_2O} C_{H_2O} \text{ (Case I)} \\ \frac{dC_{CH_4}}{dt} &= \alpha r_1 - \beta_{CH_4} C_{CH_4} \\ \frac{dC_{O_2}}{dt} &= 2\alpha r_1\end{aligned}$$

while in Case II the condition $C_{H_2O} = C_{H_2O,sat}$ is retained.

This formulation makes it possible to explore whether selective methane withdrawal improves reactor behavior, and under which conditions that improvement becomes significant.

Throughout the activity-intensification analysis, the membrane parameters were kept constant while k_1 was varied. This choice allowed the simulations to distinguish between two effects: the intrinsic increase in methane formation caused by a more active photocatalyst and the additional benefit, if any, produced by removing methane from the reactor as product accumulation becomes more significant.

3.7. Numerical Implementation and Performance Metrics

The model was implemented through explicit time stepping and used primarily for comparative sensitivity analysis. Time-step sensitivity tests were performed prior to the main simulations in order to select a discretization that provided stable results while preserving practical computational manageability. Based on these tests, a time step of 30 s was adopted for the simulations reported here. Unless otherwise stated, the calculations were performed using the parameter set summarized in Table 3. In this way, the simulations were conducted by changing only the specific variables under analysis: reactor height, water-availability scenario, membrane activation, and the apparent methane-formation constant k_1 .

Table 3. Model parameters used in the simulations.

Parameter	Symbol	Value	Unit/Comment
Time step	dt	30	s
Simulation time	t_f	48	h
Temperature	T	298	K
Gas constant	R	0.08314	L bar mol ⁻¹ K ⁻¹
Total initial pressure	$P_{tot,0}$	1.01325	bar
Water saturation pressure at 298 K	$P_{H_2O,sat}$	0.03139	bar
Initial saturated water concentration	$C_{H_2O,sat}$	1.26697×10^{-3}	mol L ⁻¹
Initial CO ₂ concentration	$C_{CO_2,0}$	3.96299×10^{-2}	mol L ⁻¹
Reactor internal diameter	D	0.1	m
Reactor radius	r	0.05	m
Reactor heights	h	0.005,	m
		0.010,	
		0.050	
		0.0393,	
Reactor gas volumes	V	0.0785,	L
		0.3927	
Illuminated base area	A_{ill}	7.854×10^{-3}	m ²
Nominal catalyst mass	W	1.0×10^{-3}	kg
Activity factor	f_{act}	1	dimensionless
Effective catalyst mass	W_{eff}	1.0×10^{-3}	kg
CO ₂ adsorption constant	K_{CO_2}	1	bar ⁻¹
H ₂ O adsorption constant	K_{H_2O}	1	bar ⁻¹
CH ₄ adsorption constant	K_{CH_4}	1	bar ⁻¹
O ₂ adsorption constant	K_{O_2}	1	bar ⁻¹
Baseline methane-formation constant	k_1	0.01	mol kg ⁻¹ s ⁻¹
Intensified methane-formation constants	k_1	0.05, 0.10	mol kg ⁻¹ s ⁻¹
Effective equilibrium-like parameter	$K_{eq,1}$	100	dimensionless
Methane extraction coefficient	β_{CH_4}	1.0×10^{-4}	s ⁻¹
Characteristic methane extraction time	$1/\beta_{CH_4}$	1.0×10^4	s, approx. 2.8 h
CH ₄ /CO ₂ membrane selectivity	S_{CH_4/CO_2}	100	dimensionless
CH ₄ /H ₂ O membrane selectivity	S_{CH_4/H_2O}	10,000	dimensionless
CO ₂ extraction coefficient	β_{CO_2}	1.0×10^{-6}	s ⁻¹
H ₂ O extraction coefficient	β_{H_2O}	1.0×10^{-8}	s ⁻¹
O ₂ extraction coefficient	β_{O_2}	0	s ⁻¹

A key issue in membrane-assisted operation is that the methane present inside the reactor is no longer identical to the methane formed by reaction, since part of the product may leave the reactor through the membrane. For this reason, methane accumulation inside the reactor was not used as the sole performance descriptor. Instead, methane formation was evaluated primarily through oxygen accumulation. Under the stoichiometry of the main methane-forming reaction, and in the absence of oxygen extraction or oxygen-consuming secondary pathways, the total methane formed can be inferred directly from oxygen production as

$$n_{CH_4,formed} = \frac{n_{O_2}}{2}$$

This quantity was used together with the methane inventory remaining in the reactor and the apparent CO₂ depletion to distinguish among methane formation, methane retention, CO₂ that specifically was transformed to methane and reactor-scale inventory effects.

To assess the usefulness of methane-selective extraction, the concept of a membrane relevance threshold was introduced. In the present work, this threshold refers to the reactor thickness, reaction time, or operating condition at which membrane-assisted methane

removal begins to produce a measurable benefit relative to the non-membrane case. This framework was used to determine whether methane-selective extraction is always beneficial, or whether its usefulness emerges only once CH_4/O_2 accumulation becomes sufficiently important to have an effect on the kinetic environment of the reactor.

For reproducibility, Table 3 reports the complete set of geometric, kinetic, adsorption, membrane, initial-condition, and numerical parameters used in the simulations. These values define the reference phenomenological scenario used throughout the study. The parameter set was not intended to represent a calibrated description of a specific photocatalyst or membrane material; rather, it provides a consistent basis for comparing the relative effects of water availability, reactor thickness, photocatalyst activity, and methane-selective extraction under controlled model conditions.

4. Conclusions

This work investigated idealized methane-selective extraction in batch photocatalytic CO_2 -to- CH_4 conversion from a reactor-level perspective. A phenomenological Langmuir–Hinshelwood-based model was used to evaluate how reactor thickness, water availability, photocatalyst activity, and methane removal interact to determine apparent CO_2 conversion, methane accumulation, and cumulative methane formation under a defined reference parameter set. The analysis does not aim to provide absolute predictive performance for a specific photocatalyst, but to identify reactor regimes in which methane accumulation and selective extraction become relevant. The analysis shows that the relevance of idealized methane-selective extraction is not universal, but depends strongly on the regime in which the photoreactor operates.

The first important conclusion is that reactor evaluation cannot rely only on apparent CO_2 conversion. Thin reactors produce higher fractional conversion because the illuminated catalyst surface acts on a smaller gas inventory. However, thicker reactors can generate larger total amounts of methane because they contain a larger CO_2 reservoir. Therefore, conversion, methane mole fraction, and cumulative methane formation are not interchangeable metrics. Each one describes a different aspect of reactor performance, and all must be considered when assessing the practical relevance of a photocatalytic CO_2 -to- CH_4 system.

Water availability was identified as a regime-defining variable. Under finite vapor-inventory conditions, water is progressively depleted, especially in thin reactors, and this limits the ability of the system to sustain methane formation. When water is buffered at its saturation concentration, conversion and methane production increase substantially. This indicates that experimental and reactor designs for gas-phase photocatalytic CO_2 reduction should not treat water vapor only as an initial feed component; instead, they should consider how water availability is maintained during operation.

At the baseline kinetic condition, methane-selective extraction strongly decreases the methane fraction remaining inside the reactor but produces only a modest increase in total methane formation. This means that, under low-productivity conditions, methane accumulation is not yet the dominant kinetic limitation. In this regime, the membrane acts mainly as a product-withdrawal element rather than as a strong kinetic intensification tool.

The situation changes when the catalytic activity is increased. In the 5 mm reactor, increasing the methane-formation kinetic constant reveals a product-accumulation-limited regime: without membrane, increasing catalyst activity no longer produces proportional gains in conversion or methane formation. Under these intensified conditions, methane-selective extraction becomes clearly beneficial, allowing the reactor to move beyond the apparent plateau observed without membrane. Thus, the membrane relevance threshold

emerges only when the system is sufficiently productive for methane accumulation to perturb the kinetic environment.

The 50 mm reactor provides a complementary insight. Its larger gas inventory leads to much higher cumulative methane formation, even though apparent conversion remains lower than in the thin reactor. In this case, the membrane still removes methane effectively, but its kinetic impact is more modest because the larger gas volume naturally dilutes accumulated products. Therefore, high methane production in a thick reactor is driven primarily by the larger CO₂ inventory, while membrane integration remains important mainly as a route for product withdrawal and methane recovery.

A central implication of this study is that producing methane is not, by itself, enough. If CH₄ remains highly diluted in CO₂, the resulting gas mixture is not directly useful as a fuel or as a practical energy vector without additional separation or upgrading. For this reason, photocatalytic CO₂-to-CH₄ studies should report not only methane formation rates, yields, or selectivity, but also the final product composition and the feasibility of methane recovery. From this perspective, idealized methane-selective extraction remains conceptually relevant even in cases where it does not strongly increase the intrinsic reaction rate, because it provides a possible pathway to obtain a methane-enriched stream that could be used for energy storage or as a petrochemical feedstock.

Overall, the results indicate that future progress in photocatalytic CO₂-to-CH₄ conversion should couple catalyst development with reactor and separation design. More active photocatalysts will make product accumulation increasingly important, especially in small-volume reactors, and this will increase the need for in situ methane extraction. At the same time, larger-volume reactors may favor total methane production by providing a larger CO₂ reservoir, but they still require product-management strategies if the methane is to be recovered in a useful form. Therefore, the technological relevance of photocatalytic CO₂ reduction to produce methane will depend not only on forming methane selectively, but on designing reactor–membrane systems capable of producing, extracting, and concentrating methane under practically meaningful conditions.

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