EVALUATIONS ON VARIOUS PATHWAYS FOR CONVERTING CO2 INTO CHEMICALS

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Abstract

To mitigate the damage caused by climate change, significant research efforts have been made in the field of CO2 utilization. However, the existing data obtained from process analysis has still been inconsistent due to the varying levels of complexity of the models used for analysis and the different groups conducting the analysis. Aiming to accurately compares various CO2 conversion pathways, our research group is currently establishing a platform based on rigorous process simulation. With this paper, the key findings from our recent studies in the field of CO2 utilization are summarized and compared.

**Keywords**: CO2 utilization, process simulation, techno-economic analysis, decarbonization, rigorous model.

* 1. Introduction

The concept of CO2 capture, utilization, and storage (CCUS) has emerged as a highly researched topic in both academia and industry, in order to mitigate excessive CO2 emissions. Among them, the utilization of CO2, which aims to convert CO2 into green and value-added chemicals, plays a key role.

The CO2 conversion pathways can be categorized as either non-reductive or reductive. The non-reductive pathways do not involve a change in the oxidation states of CO2 during the reaction. Such a process converts CO2 directly into alkyl carbonates when combined with alcohols, into aliphatic polycarbonates when combined with diols, into ureas when combined with amines, and into carbamates when combined with both alcohols and amines simultaneously (Tomishige et al., 2020; Tomishige et al., 2019). Despite their atomic efficiency, the main challenge of such processes is the issue of severe chemical equilibrium. This indicates that a suitable catalyst and an intensified reactor system may be necessary to enhance the performance of the reaction.

In contrast, reductive conversion occurs when the oxidation state of the carbon center in CO2 changes. Such pathways require the addition of a highly active co-reactant to react with CO2. Some well-known reductive pathways include the direct hydrogenation of CO2 to form hydrocarbons (e.g. methane, syngas, and liquid fuels), the reaction with epoxide to form carbonates (e.g. ethylene carbonate, by reacting with ethylene oxide), and so on. Overall, the reductive reactions can proceed more easily. However, incorporating an additional co-reactant, especially hydrogen, leads to economic barriers.

There have been several previous studies aimed at evaluating various CO2 conversion processes, primarily in terms of their economic viability and potential for decarbonization. However, some issues have remained unresolved. First, simplified process models were used for performance evaluation in many previous studies. The alternative process configurations have not been the main focus of study, either. This limits the results obtained from the analysis. Second, different research groups used different process models for analysis. This causes the evaluation results to diverge and lacks a consistent basis. To address this issue, our research group has been developing a rigorous simulation-based framework that presents the most recent discoveries in various CO2 conversion processes. Within this framework, different CO2 conversion processes can be compared on a fair basis. In this paper, the important findings from our recent studies are summarized.

* 1. Rigorous Modeling of CO2 Utilization Processes

This section highlights the selected processes. To conduct rigorous process simulation, special attention has been paid to the kinetics and thermodynamics, which are the foundation for designing the reaction and separation sections, respectively. Aspen Plus V12 was used for process modeling. The economic feasibility (using the minimum required selling price, or MRSP, in USD/kg) and decarbonization potential (measured by the amount of CO2 emissions per unit of product formed, or CO2-e, in kg/kg) of each process can be evaluated and compared together. The specific details of each process can be referred to as indicated.

* + 1. Reductive conversion pathways

2.1.1 Synthesis of methane

Methane can be synthesized from direct hydrogenation of CO2. In a recent paper by Uddin et al. (2022), eight alternative configurations based on fixed-bed reactors were developed and compared. The proposed schemes differ in the number of reactors and the format of heat management (e.g., adiabatic, non-adiabatic with co-current or counter-current exchange). The analysis recommended the use of a two-reactor configuration, with the first stage being a non-adiabatic reactor equipped with internal recycle and counter-current cooling, and the second stage being an adiabatic reactor. A suitable control strategy for this process configuration was also proposed.

2.1.2 Synthesis of methanol

In the context of CO2 utilization, methanol can be produced by reacting the CO2 captured from waste gas (such as flue gas) with green hydrogen (generated from the electrolysis of alkaline water). Recently, Chiou et al. (2023) proposed six commercially viable reactor configurations for CO2-based methanol process and evaluated them in terms of MRSP (in USD/kg) and CO2-e (in kg/kg). The recommended configuration is to use two reactors. The first stage should be an adiabatic reactor with current-cooling, followed by another adiabatic reactor. A suitable control strategy was also developed for the selected scheme.

2.1.3 Synthesis of dimethyl carbonate

Yu et al. (2018) proposed two processes that convert CO2 into dimethyl carbonate (DMC). The first process follows an indirect and reductive pathway. It reacts CO2 with ethylene oxide (EO) to form ethylene carbonate (EC) in the first step, while it further reacts EC with methanol (MeOH) to form DMC and ethylene glycol (EG) in the second step. The second process proposed reacting CO2 directly with MeOH to form DMC and water, with the addition of butylene oxide (BO) as a chemical dehydrant. As reported in this paper, the first process is superior to the second due to its higher per-pass conversion of CO2. Although the second process incorporated in situ water removal, the per-pass conversion can only be enhanced to around 10%. This leads to the heavy separation tasks following the reaction section. However, although the first process can be economically viable, it did not show promise in terms of decarbonization (CO2-e = +0.049), even with the implementation of the extreme heat integration strategy. The main cause is the separation of the azeotrope between MeOH and DMC. As the azeotropic composition leans towards the pure MeOH end, the separation of this azeotrope requires distilling a large amount of lighter species to the distillate, thereby resulting in high energy consumption.

2.1.4 Synthesis of glycerol carbonate

Wu et al.(2024) proposed a novel process for producing glycerol carbonate (GC) through the indirect conversion of CO2. The process converts CO2 and propylene oxide (PO) into propylene carbonate (PC) in the first step, while further converting PC with glycerol (GLY) to GC and a co-product, propylene glycol (PG), subsequently. This paper also proposes using GC as a heavy entrainer, enabling the separation of the close-boiling PC and PG through extractive distillation. This method would simultaneously facilitate the purification of PG and the recycling of unreacted PC. Based on the findings, we have concluded that this process shows promise in both economics (MRSP = 0.628 USD/kg) and decarbonization (CO2-e = -0.238). Considering the appealing properties of GC and its favorable process analysis results, further development of this process is recommended.

2.1.5 Other possibilities

There are still many potential pathways to produce chemicals through the reductive conversion of CO2. For example, the production of hydrocarbons (either light or heavy) through Fischer-Tropsch synthesis and higher-order alcohols has been investigated both experimentally and computationally. Note that most of the well-known reductive conversion processes of CO2 produce commodity chemicals. Their features include fewer barriers in production, a large scale of production, and a lower unit price for the products. As the processes incorporate expensive co-reactants, there is a growing trend towards exploring reductive conversion to produce more valuable components.

* + 1. Non-reductive pathways

2.2.1 Synthesis of alkyl carbonates

A globally renowned team in the field of non-reductive conversion of CO2, led by Tomishige et al. at Tohoku University, has proposed over fifty viable pathways for directly converting CO2 into carbonates, carbamates, or ureas (Tomishige et al., 2020; Tomishige et al., 2019). However, it can be impractical to perform rigorous simulations and comprehensive analyses for all of these processes. To identify processes with potential both in economics and decarbonization, Lee et al. (2021) proposed a screening method based on thermodynamics and process understanding. There are three rules for the screening: (1) No azeotropes or close-boiling behavior should form between the reactants and the products; (2) high selectivity towards the product should be reported from the experiment; (3) the reacting conditions should be industrially relevant. The pathways that meet these three screening rules can be highly productive while emitting a lower amount of indirect CO2 emissions during the separation of reactor effluents.

Lee et al. (2021) analyzed 15 pathways that convert CO2 into various carbonates and carbamates using these screening rules. Relevant experiments were conducted using a highly efficient CeO2 catalyst with the addition of 2-cyanopyridine (2-CP) to facilitate *in situ* water removal (Tomishige et al., 2019). There are four process pathways that pass the screening step, including the production of dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate (DPC), and isopropyl n-phenyl carbamate (IPPhCM). The process models for these four processes were thereby developed, which subsequently served as the basis for conducting techno-economic and decarbonization analyses. As indicated from this study, the production of DEC can be appealing in both economics (MRSP=2.38 USD/kg) and decarbonization (CO­2-e = -0.154).

The key aspect of whether these processes can be further scaled up lies in the regeneration of 2-CP. As mentioned by Honda et al.(2013), the regeneration of 2-CP proceeded very slowly in a solvent. To investigate this issue, Yu et al. (2020a) obtained the most extreme operating conditions for the regeneration section of the DEC process which resulted in the overall process becoming carbon neutral. In general, the issues surrounding the handling of 2-CP have sparked new discussions on non-reductive conversion pathways. If 2-CP is not regenerated, it could be crucial to find ways to manage the hydration product, 2-picolinamide (2-PA). Besides, it is also necessary to find a reliable source that consistently supplies 2-CP in order to make the process feasible. Otherwise, it is urgently necessary to develop a more suitable reaction system that efficiently regenerates 2-CP. Relevant discussions can also be referred to in a more recent paper by Huang et al. (2023).

2.2.2 Synthesis of isopropyl n-phenyl carbamate (IPPhCM)

The production of IPPhCM was further investigated by Huang et al. (2023), with more rigorous description of the reaction kinetics and reactor configurations. Due to the numerous side reaction occurring the system, the optimal operating conditions were obtained based on different combinations of conversion and yield. With proper strategies for heat integration and thermal coupling, and the addition of ammonia into the reactor to facilitate the regeneration of side products, the process can achieve an exergy efficiency of 71.8% while slightly producing net CO­2 emissions (CO2-e to +0.118 kg/kg).

2.2.3 Synthesis of polycarbonates

Another process that produced poly(butylene carbonate) by reacting CO2 with 1,4-butanediol was proposed by Yu et al. (2020b), based on the previous experimental findings reported by Tomishige et al. The original experiment involved excessive use of solvents (methanol and tetrahydrofuran) and a scrubbing agent (water), making the separation section of this process highly energy-intensive. To make this process achievable, it is necessary to reduce the amount of solvent used.

2.2.4 Other possibilities

Since the non-reductive conversion processes mentioned above involved the use of a chemical dehydrating agent (i.e. 2-CP), this complicates the separation processes and also leads to undesired side reactions. Exploring alternative pathways or reacting systems that can proceed with fewer chemical equilibrium limitations may still be recommended.

* 1. Results and comparisons

The evaluation results for all the processes mentioned in Section 2 are summarized **Table 1**. The readers may refer to the indicated papers for more details. The MRSPs (i.e., calculated at a 15% internal rate of return) for producing each chemical are compared with its current market price. The CO2-e of the designed scenario are compared with the theoretical values, both with and without consideration of the footprint of CO2 capture. A negative value of CO2-e indicates that the overall process in is net decarbonization. The theoretical CO2-e can be calculated directly from the reaction formula, representing the theoretical amount of CO2 (in kg) required to produce one kg of the product.

**Table 1**. Comparisons of MRSP and CO2-e for various CO2 conversion processes.

|  |  |  |
| --- | --- | --- |
|  | Economics (USD/Ton) | CO2-e (kg/kg) |
|  | MRSP | Market | Design(w/o footprint) | Design (w/ footprint) | Theoretical |
| Reductive |
| Methane | 32.80a | 2.03-6.49a | -3.338 | -2.777 | -2.750 |
| MeOH | 986 | 322-434 | -1.254 | -0.974 | -1.375 |
| GC | 628 | 2400 | -0.238 | -0.162 | -0.373 |
| DMC | 768 | 690 | 0.054 | 0.154 | -0.488 |
| Non-Reductive |
| DMC | 1500-4960 | 690 | 0.049 | 0.149 | -0.488 |
| DPC | 2070-4060 | 3000 | 0.088 | 0.149 | -0.301 |
| PBC | 1580b | n.a. | 4.340 | 4.417 | -0.379 |
| DEC | 1120-2810 | 1100-1900 | -0.237 | -0.161 | -0.372 |
| IPPhCM | 1759 | n.a. | 0.118 | 0.168 | -0.246 |

aIn a unit of USD/MMBTU; bThe yearly manufacturing cost is listed.

**Table 1** shows that products produced through direct hydrogenation (i.e., methane and methanol) have significantly higher MRSP compared to their market prices. The main reason is the inclusion of green hydrogen, which costs 2.4 USD/kg. It is also concluded that such processes can be economically comparable to the existing processes only if green hydrogen is available at a low to moderate cost. In addition, the two indirect processes that produce GC and DMC by reacting epoxides with CO­­2 show better economic viability. However, the value of MRSP may change as the costs of the co-reactants and the values of the co-products vary.

There have been few cost data available to compare the MRSPs of the product generated through non-reductive pathways. Within the limited data, the MRSP of DMC was found to be much higher than its market price. The necessary separation of high-boiling species related to 2-CP and its derivative should be the main cause. For the other chemicals, the MRSPs of DEC and DPC generally lie within the range of the corresponding prices. No existing data can be used to compare the MPSPs of IPPhCM and PBC.

In terms of decarbonization, it is generally observed that each process has a higher CO2-e value than its theoretical value. This is because indirect emissions produced by utility consumption are considered. The methanation process is an exception. In this process, the steam generated through waste recovery is more than sufficient to meet its own requirements. The recovered waste heat can be used in other processes, thereby resulting in further reduction in CO2 emissions. Note that the theoretical CO2-e is lower if producing molecules with larger molecular weight. Hence, the overall CO2-e may become positive if the separation section consumes a significant amount of energy, even if the process uses CO2 as the starting material.

Considering the carbon footprint associated with CO2 capture, the results of decarbonization analysis may become less favourable. Here, the calculation incorporated the emission data for the commercially available CO2 capture process using monoethanolamine (MEA) solution. This includes an average specific energy consumption of 2.8 GJ/Ton-CO2, and 0.204 kg of indirect CO2 emissions per kg of CO2 captured. The inclusion of this term causes the slightly negative CO2-e of certain processes to become positive.

There are still many factors to consider when providing comprehensive evaluations of CO2 conversion processes. For example, Chiou et al. (2023) pointed out the trade-off between economics and decarbonization caused by the utilization of various hydrogen sources. Huang et al. investigated the economic uncertainties resulting from the incorporation of 2-CP as a dehydrant in the production of IPPhCM. Yu et al. (2020a) and Lee et al. (2021) conducted a series of sensitivity tests to investigate the impact of varying unit prices on the MRSPs. Although the various items were investigated in different studies, the use of a rigorous model ensures that all the analysis results are comparable.

Note that comparing the MRSP and CO2-e of the proposed processes provides a unified approach to their evaluation. This also makes the framework flexible for comparing the newly proposed CO2-based processes to the previous ones.

* 1. Conclusions

This paper summarizes our recent findings of various CO2 conversion processes (i.e. th e production of methane, methanol, various carbonates, n-phenyl carbamate, and poly(butylene carbonate). Within this framework, different CO2-based processes were rigorously developed and were compared on a fair basis. In the foreseeable future, our research team aims to develop an integrated platform that will disclose the latest simulation-based analysis of various CO2 conversion processes. The rigorous models used for process analysis will be made open to the public to provide a consistent basis.

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