




REVIEW

Carbon dioxide utilization: A critical review from multiscale perspective

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Abstract

Carbon dioxide (CO₂) emissions contribute considerably towards increasing greenhouse effect. Carbon capture and storage can reduce CO₂ emissions to a great extent but lacks economic feasibility. The economic feasibility of CO₂ capture could be boosted by utilizing the captured gas to produce valuable end products. CO₂ is a highly stable molecule; therefore, special catalysts and elevated conditions of temperature and pressure are required for its conversion. This review presents the current status of CO₂ utilization processes from various aspects, including thermodynamic, economic, and environmental impacts. The use of process systems engineering (PSE) tools and techniques in a broad spectrum, to improve the technical, economic, and environmental feasibility of these processes, is the major focus of this review. In this regard, a framework has also been presented showing the integration of various PSE techniques. All the related information in the form of tabulated data as well as qualitative and quantitative plots have been presented and critically analyzed.

KEYWORDS

chemical conversion, climate change mitigation, CO₂ utilization, greenhouse gas emissions, process systems engineering, sustainability

1 | INTRODUCTION

The high concentration of carbon dioxide (CO₂) in the stratosphere hinders the formation of new ozone molecules and therefore, contributes toward greenhouse effect.¹ Moreover, the concentration of CO₂ is continuously increasing in the atmosphere contributing extensively toward global warming.² The advent of first industrial revolution in Europe and the United States, in the period from 1750 to 1850 led to a negligible rise in the global CO₂ emissions. But afterward, rapid growth of industrialization in the world caused a significant increase in CO₂ emissions, especially from anthropogenic sources.³ The atmospheric growth of CO₂ was 2.04 GtC/yr (giga ton carbon per year) in 1959 that followed an oscillating behavior with an ultimate increase to 5.43 GtC/yr in 2019⁴ as shown in Figure 1. National Oceanic and Atmospheric Administration (NOAA) and American Meteorological Society (AMS) reported the global atmospheric CO₂ concentration as 407.4 ppm in 2018, that was about 2.5 ppm more than that in 2017.⁵ In May 2019, for the first time in the history, sensors measured the atmospheric CO₂ concentration to be around 415 ppm that is substantial when compared to 240 ppm some thousand years ago.⁶ Burning of fossil fuels for transportation, industry, and power generation causes significant increase in CO₂ concentration in the environment. Power generation and transport accounts for over 67% of the rise in anthropogenic greenhouse gas emission (GHGs) emissions.⁷ The worldwide increase in power demand has caused significant increase in the consumption of coal, oil, and natural gas which in turn accelerated the CO₂ emissions.

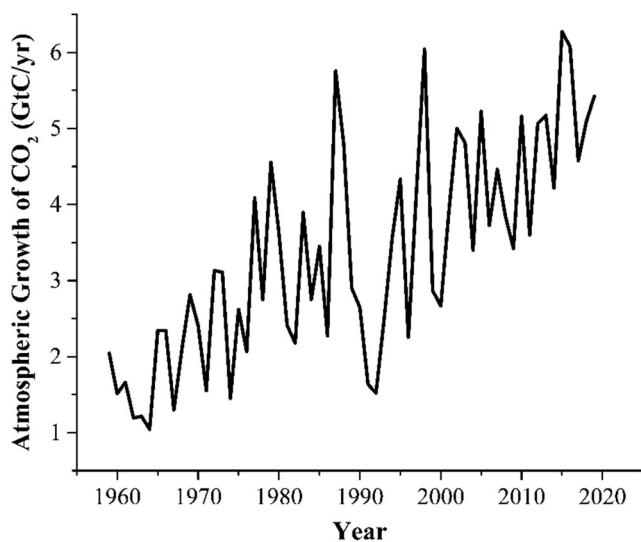


FIGURE 1 Atmospheric growth of CO₂. Source: Reproduced from Friedlingstein et al.⁴

The GHGs (prominently CO₂) emissions can be reduced by following these four possible pathways: (1) increasing the efficiency of existing appliances, plants, and processes, (2) replacing the fossil fuel-based technologies to renewables or low CO₂-based technologies, (3) carbon capture and storage (CCS), and (4) carbon capture and utilization (CCU). Improving the efficiency of existing mature processes is not an easy task as most of the already installed processes have little space for further improvement.⁸ Renewable energy technologies like solar and wind are now developed and are cost competitive to fossil fuels.⁹ However, an important concern associated with these renewable energy resources is their intermittent nature.¹⁰ Moreover, efforts are in progress to replace fossil fuel-based power plants and synthesis gas generation units to biomass-based processes in order to reduce GHGs emission. However, biomass-based fuels have low energy density and are mostly preferred as a combined fuel mixed with coal. To overcome this issue, a reasonable share of conventional power generation is required owing to its continuous availability and suitability to meet peak load demands. Furthermore, fossil fuels are an important feedstock for a variety of chemicals and fuels. Therefore, CO₂ mitigation technologies will be required to mitigate the environmental damage by associated emissions with the burning/utilization of fossil fuels.

Carbon capture can be implemented in shorter span both on existing and new power plants.¹¹ However, the underground storage of CO₂ may create surface stability issues or false permeation leading to leakages and thus, emitting the captured CO₂ back to the atmosphere.¹² However, these leakages could be reduced by continuous monitoring of CCS sites.¹³ Furthermore, CCS is a cost intensive process and it affects the plant economy to a great degree as the cost of electricity (COE) is increased from 45% to 70% depending on the type of fuel and plant.¹⁴ CO₂ utilization is now considered as the most feasible option available and focus is shifting toward the production of valuable products from CO₂.¹⁵ It could significantly help to reduce the cost of CO₂ storage as well as recover the cost of carbon capture, and can improve the overall economy of the process.¹⁶ Integration of CO₂ capture process with some of the CO₂ utilization processes (e.g., hydrogenation of CO₂ to methanol) and doing energy integrations, the energy required for capture process can be reduced thus reducing the cost of CO₂ capture.^{17,18} Currently, the CO₂ utilization processes require energy input in the form of heat, pressure and/or catalyst for the activation of highly stable CO₂ molecule, this is the reason behind the economic infeasibility of most of CO₂ utilization processes. Nevertheless, CO₂ utilization processes could be

made sustainable by employing computational techniques at multiscale levels such as optimizing the operating and design parameters, selection of reaction pathways, process integrations, using renewable energy sources and utilizing the waste heat of processes.

Apart from the mitigation techniques discussed above, GHG emissions could also be abridged by optimizing the energy mix of the country, with the intention to minimize cost and GHG emissions.¹⁹ However, this is a long-term solution, requires significant finance flows and has certain assumptions associated with it. The choice of the utilization process depends on the following factors: (1) CO₂ availability, (2) product demand, (3) product price, (4) process economics, and (5) overall environmental impact. The main objectives of the CO₂ utilization process are net CO₂ and cost reduction.²⁰ Various studies on CO₂ utilization routes have been reported in the literature. Utilization of captured CO₂ is mainly in the (1) production of carbon-neutral fuels that do not emit net CO₂ on combustion, for example, methanol^{17,21–23}; (2) synthesis of various chemicals, for example, polycarbonates,²⁴ acetic acid,²⁵ urea,²⁶ and many others; (3) enhanced oil recovery (EOR) process,²⁷ where captured CO₂ is injected in depleted oil wells giving up to 40% increased oil production; (4) synthesis of biofuels with micro algae,²⁸ that can be used as a source of energy; (5) CO₂ can also be utilized through photosynthesis by growing more plants²⁹ resulting in more biomass production; and many other processes. In recent years, several review articles have been published with focus on several aspects such as photocatalytic CO₂ reduction,^{30,31} CO₂ utilization through carboxylation and reduction reactions,³² hydrocarbon and methanol synthesis,³³ assessing early-stage CO₂ utilization technologies,³⁴ current status, challenges and roadmap for the further development of CO₂ utilization technologies,^{35–37} cultivation of microalgae using CO₂ and hydrogenation of CO₂ to energy products,³⁸ advanced chemical looping materials (i.e., metal oxide-based materials) for CO₂ utilization,³⁹ review of patents on CO₂ utilization technologies published between 1980 and 2017,⁴⁰ overview of reaction mechanisms and catalyst activities for CO₂ utilization,⁴¹ process systems perspectives,⁴² and life cycle environmental impacts.⁴³

The published review articles are limited, and various articles presented some selected options for CO₂ utilization. Mature technologies, emerging technologies, and innovative explorations are presented with major focus on the reaction mechanisms, catalysts and their activities, operating conditions, and yield of the product. However, the review on the use of computational techniques for the assessment, improvement and

innovation of certain processes or products is limited. In this context, the published article focusses on the process level simulations and other computational techniques such as molecular level simulations, computational fluid dynamics (CFD), life cycle assessment (LCA) and process or superstructure level optimizations were not reported. Moreover, autonomous discussion of process modeling and simulation techniques was not spotted. The systematic approach in PSE perspective can be very useful for the accelerated development and innovation of the CO₂ utilization.

In this article, a comprehensive review of CO₂ utilization processes with special focus on current status of the recent process and operating developments including performance of the catalyst; effect of operating conditions; reduction in the energy demand; utilization of renewable energy; overall cost reduction; carbon footprint reduction; and the PSE perspectives in process selection, design and optimization is presented. As the selection of a CO₂ utilization process (for further research or industrial implementation) is a critical decision, many process parameters like lifecycle inventory, CO₂ reduction potential, energy requirements, catalyst requirement, and process economics must be thoroughly considered. The specific details are presented in a systematic way to help researchers become aware of the current status of the developments and challenges as well as the vast array of possible solutions. The scope of this paper does not include the details on carbon capture technologies as several review articles^{44–48} are already available in the literature. A review of the studies involving the use of computational tools to analyze the CO₂ capture as well as its utilization processes is presented, under the umbrella of five different computational techniques; molecular level simulations, CFD, LCA, process or plant level simulations and process optimization, to give greater insights about these processes.

The rest of the paper is organized as follows. The second section presents a detailed discussion on options for CO₂ utilization (including physical and chemical processes) along with their performance analysis and related issues. A wide spectrum of the PSE perspective (starting from molecular level simulations to superstructure level optimization) in exploring, analyzing, selecting, designing, and integrating the CO₂ utilization processes is presented in the third section along with a framework presenting the integrated use of these PSE techniques to maximize the thermodynamic, economic, and environmental benefits from these processes. Finally, conclusions are presented followed by future recommendations.

2 | CARBON DIOXIDE UTILIZATION

CO₂ utilization processes are broadly classified into two categories: physical utilization and chemical utilization. Among various physical utilization processes, the most prominent ones are presented in Figure 2. Some physical utilization processes like EOR and enhanced gas recovery (EGR) are also termed as CO₂ sequestration because of their potential to store large volumes of CO₂.⁴⁹ CO₂ has the potential to be utilized chemically in the production of fuels and chemicals including ethanol, di-methyl carbonate (DMC), di-methyl ether (DME), methanol, methane, syngas and carbonates. In this article, major focus is given to chemical utilization processes because of their potential to abate CO₂ (by changing the molecular identity) as most of the physical utilization processes stores CO₂ for small period of time (e.g., dry ice, fire extinguishers and carbonated beverages). However, a brief discussion about physical utilization processes is added in Section 2.1. Moreover, literature regarding use of PSE techniques in development of physical utilization processes is also included in Section 3. The purpose of this section is to make the readers aware of various options that can utilize CO₂. For this purpose, a brief review of various physical and chemical utilization processes is presented in this section with major focus

on the current status, recent advances, CO₂ mitigation potentials, and related issues or challenges.

2.1 | Physical utilization

During physical utilization, CO₂ remains in pure form either suspended in a solution or have its own distinguished existence. These processes exploit the physical properties of CO₂ for its utilization, for example, solubility of CO₂ endorsed its use in carbonated beverages. Numerous industrial applications are known in which CO₂ can be physically consumed; prominent ones are sketched in Figure 2. This section presents the processes for physical utilization of CO₂ as well as pros and cons along with technology readiness levels (TRLs) as given in Table 1. The main types of physical utilization include EOR, EGR, enhances geothermal systems, carbonated beverages, dry ice and fire extinguishers.

2.2 | Chemical utilization

In contrast to physical utilization, the CO₂ molecule's identity in chemical utilization does not exist in the end products as it is transformed into some other compound. CO₂ is extensively used in chemical industry especially as

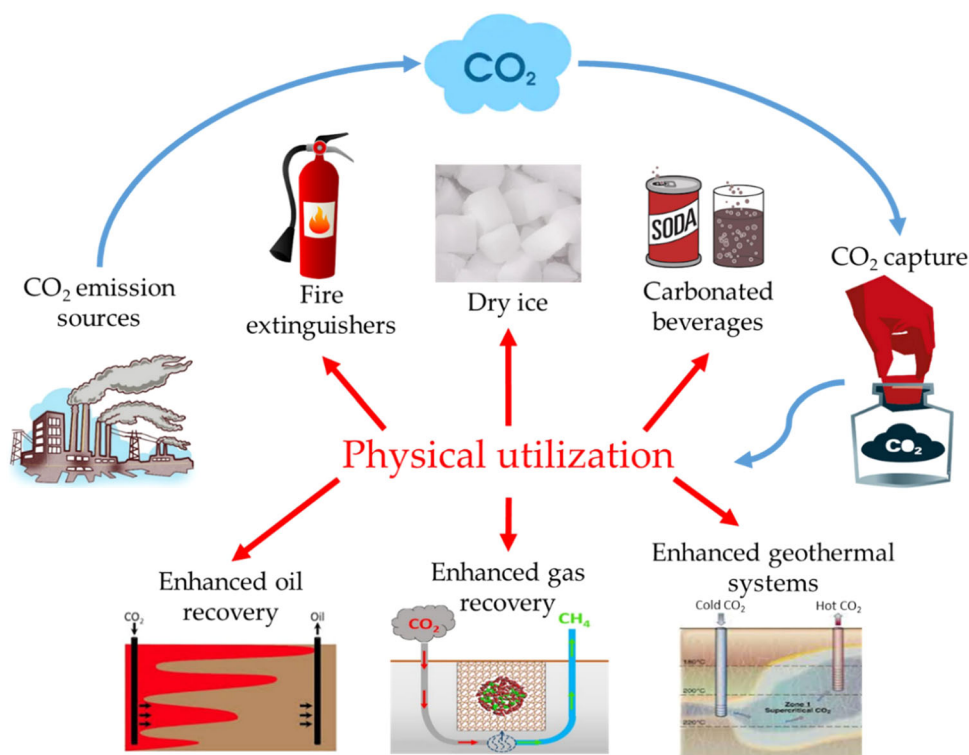


FIGURE 2 Physical CO₂ utilization processes

TABLE 1 Summary of various physical CO₂ utilization processes

Utilization/ sequestration option	Pros	Cons	TRL
Enhanced oil recovery	<ul style="list-style-type: none"> • Large volume of CO₂ can be sequestered permanently • Increases oil production from oil fields • Economically favorable process especially when carbon tax is implemented 	<ul style="list-style-type: none"> • Due to low viscosity of CO₂ oil recovery is less compared to other working fluids • The trapped CO₂ in the wells can leak back to the atmosphere which is a serious concern 	9
Enhanced gas recovery	<ul style="list-style-type: none"> • Large volume of CO₂ can be sequestered permanently • Increased gas production from gas wells • Due to density and viscosity differences, mixing of CO₂ and CH₄ can be avoided (at high methane concentrations) 	<ul style="list-style-type: none"> • Separation of natural gas from injected CO₂ (when natural gas concentration is low) is an issue and requires additional processing • The trapped CO₂ in the wells can leak back to the atmosphere which poses a serious concern 	9
Enhanced geothermal systems	Compared to water: <ul style="list-style-type: none"> • Increased heat recovery from hot rocks • CO₂ leakage in rocks is favorable as it do not create stability issues 	<ul style="list-style-type: none"> • Very deep drilling is required for EGS • Economically infeasible for commercial applications 	5
Carbonated beverages	<ul style="list-style-type: none"> • Adds value to beverages taste • Consumption of CO₂ in beverages can improve capture process economy 	<ul style="list-style-type: none"> • No sequestration of CO₂ • Too much consumption of carbonated beverages has serious health impacts 	9
Dry ice	<ul style="list-style-type: none"> • Dry ice has got advantage of lower temperature than ice • It does not leave any residue behind (like water in case of ice) 	<ul style="list-style-type: none"> • Too much lower temperature is dangerous • Ultimate addition of CO₂ to the atmosphere when it sublimates 	9
Fire extinguishers	<ul style="list-style-type: none"> • Good fire extinguishing characteristics • Best suited for electrical fires • No harmful residues left behind 	<ul style="list-style-type: none"> • Ultimate addition of CO₂ to the atmosphere • They cannot be used for solid fuel burning fires 	9

a feedstock for the production of various chemicals and synthetic fuels. CO₂ is a highly stable compound of carbon and significant energy inputs (in the form of high temperature and pressure) are required for its chemical conversion. However, requirement of elevated conditions can be reduced by the addition of process-specific catalysts. Most of the reactions of CO₂ are carried over metallic catalysts and still high temperature and pressure conditions are required for its conversion. However, economics of the reaction pathways using CO₂ can be improved by (1) developing new catalysts which reduces the energy requirement of the reactions, (2) optimizing the design and operation of the utilization processes, (3) utilization of renewable energy to save the energy cost and reduce GHG emissions, and (4) exploring new pathways and reactants for CO₂ utilization as huge volumes of CO₂ are continuously being released to the atmosphere due to burning of fossil fuels. This requires special focus of researchers from various fields to develop novel processing routes for abatement of atmospheric CO₂. Moreover, in doing economic analysis or energy conservation, the net reduction in overall CO₂ footprint should be realized along with economic benefits.

Several options are available to convert CO₂ chemically into useful products. Several prominent chemical utilization pathways are critically reviewed in this section. The current focus is on finding the most beneficial pathway (in terms of economic and environmental impacts) to utilize CO₂. Selection of CO₂ utilization process for its implementation is a critical decision. Most important parameters that must be analyzed before selection of CO₂ utilization process includes market demand of the end product, CO₂ reduction potential, raw material availability, and economic feasibility.

Annual production of various chemicals and fuels along with their stoichiometric CO₂ uptake potentials and TRLs (if produced by CO₂ conversion) are presented in Table 2. Stoichiometric CO₂ uptake potentials of these chemicals and fuels presents that out of all the target compounds (presented in Table 2), theoretically methane production has the highest potential to utilize CO₂. It should be realized that these stoichiometric CO₂ uptake potentials does not incorporate the emissions associated with processing intervals; however, these data may provide an overview of reduction in CO₂ emissions if environmental friendly routes could be developed for

TABLE 2 Summary of chemical utilization options

Compound	Production (Mt/yr)	Specific mass (ton CO ₂ /ton product)	Stoichiometric CO ₂ uptake (MtCO ₂ /yr)	TRL	Reference
Acetic acid	10.25	0.733	7.513	3	[50]
Acrylic acid	5.85	0.611	3.574	3	[51]
Algae	35	1.8	63	7	[52]
Calcium carbonate	113.9	0.439	50.00	7	[37]
Carbamates	5.3	--	>6	2	[37]
Dimethyl carbonate	1.60	1.466	2.346	5	[52]
Dimethyl ether	11.4	1.911	21.785	3	[37]
Ethanol	80	1.911	152.88	2	[52]
Ethylene carbonate	0.2	0.499	0.099	8	[52]
Formaldehyde	21	1.45	30.45	3	[37]
Formic acid	1.0	0.956	0.956	6	[53]
Magnesium carbonate	20.5	0.261	5.350	4	[52]
Methane	1100-1500	2.75	3025-4125	7	[52]
Methanol	65	1.373	89.245	9	[52]
Polycarbonates	5	0.173	0.865	9	[53]
Polyurethane	15	0.3	4.5	9	[52]
Propylene carbonate	0.2	0.431	0.086	7	[52]
Salicylic acid	0.17	0.319	0.054	9	[54]
Sodium carbonate	62	0.415	25.73	6	[55]
Synthesis gas	359	1.4667	526.545	6	[56]
Urea	180	0.735	132.3	9	[57]

CO₂ utilization. Production of urea, dimethyl carbonate, methanol, polycarbonates, polyurethane, and salicylic acid are the mature technologies. It should be noted that Table 2 presented an assessment of reduction in CO₂ achieved if all the current production of target product is from CO₂. For example, most of the methane is naturally extracted and its related production terms in Table 2 include production from all sources including natural extraction. However, the stoichiometric CO₂ uptake is calculated if all the production amount of methane is manufactured from industrial process utilizing CO₂. Industrial production of methane is not a mature technology and TRL mentioned here is for the industrial process that can utilize CO₂. Furthermore, the production terms presented in Table 2 contain current overall production which may be increased if the economy of CO₂ utilization improves.

The important chemical utilization products include urea, syngas, methanol, DME, formic acid, methane, dimethyl carbonate, polyurethane, carbamates, microalgae,

ethanol, salicylic acid, calcium carbonate, sodium carbonate, formaldehyde, magnesium carbonate, acetic acid, acrylic acid, ethylene carbonate, propylene carbonate, and polycarbonates.

CO₂ is not permanently utilized by the process of urea production. After 8 days of application of 55.8 mg carbon as urea, 54 mg of carbon is released as CO₂.⁵⁸ This carbon footprint can be slightly reduced by using CO₂ from reformer flue gas as reactant in the process.⁵⁹ Integration of urea production plant with power plant or other CO₂ emission sources can reduce the carbon footprint by using CO₂ emitted as feedstock for urea production. A novel process for coproduction of urea and electricity from power plants was proposed in which CO₂ from flue gases of the power plant was used as raw material for urea production.⁶⁰ More than 1.68 tons of urea production was indicated per ton of CO₂ consumed. Utilization of CO₂ for urea production is a mature technology and it has the potential to mitigate significant CO₂ if coproduction processes are considered.

CO₂ can be split to CO by any of the paths based on the source of energy used that is, microwave energy, solar energy, or wind energy. Splitting CO₂ to carbon monoxide and combining it with hydrogen results in syngas.⁶¹ Syngas can also be produced by CO₂ reforming of hydrocarbons and by coelectrolysis of CO₂ and H₂O.⁶² Methanol has wide range of applications, including its use as a feedstock for production of various chemicals and its potential for use as a fuel.⁶³ CO₂ conversion to methanol is usually done by its catalytic hydrogenation. Cu/ZnO/Al₂O₃ catalyst is usually used⁶⁴ under mild conditions of temperature (210–270°C) and pressure (50–100 bar) with high selectivity of 99%.⁶⁵ Hydrogen is the main cost burden on overall economics of the methanol production. Sustainability of CO₂ hydrogenation for methanol production extremely depends upon the electricity source used for water electrolysis; use of electricity produced by renewable and nuclear energy sources to keep the net negative CO₂ emissions. Methane is particularly used as a fuel, and as a reactant in rubber manufacturing as well as in carbon black production.⁶⁶ CO₂ can be converted to methane by treating it with hydrogen at elevated temperature (300–400°C) and pressure in the presence of Ni catalyst. Methane production from CO₂ has the significant potential to reduce CO₂ emissions as shown in Table 2 but this process is not yet implemented on industrial scale as methane is currently extracted from natural reserves. Ethanol is usually considered as a renewable energy source as it is conventionally produced by fermentation of sugars.⁶⁷ Ethanol has the potential to be used as an alternative fuel.⁶⁸ Moreover, if ethanol production is carried by utilization of renewable energy source, the net CO₂ emissions by ethanol burning will be zero. Ethanol has the potential to be used as an environment friendly fossil alternative fuel but CO₂ conversion to ethanol is currently facing challenges regarding catalyst activity and process design.

Recently, much focus has been given to DME production because of its potential for use as a diesel alternative green fuel as its combustion results in comparatively less GHG emissions.⁶⁹ Coproduction of electricity and DME is an emerging field as it can replace significant proportion of fossil fuels with DME (a diesel alternative fuel) accompanying CO₂ mitigation. CO₂ can also be converted to formic acid by its electrochemical reduction in which coelectrolysis of CO₂ and H₂O results in methanol production (which is then converted to formic acid).⁷⁰ Currently, production of formic acid from CO₂ is not a well-developed process and special focus is needed on development of this process to take full advantage of its CO₂ reduction potential mentioned in Table 2. Electrochemical reduction route has lower TRL

than catalytic process; however, in future, commercialization of electrochemical cells will provide a means to utilize CO₂ at atmospheric conditions using the renewable energy or waste electricity from power plants. DMC is an intermediate for poly-carbonate resins production and has the potential to be used as a methylation agent.⁷¹ CO₂-based production of DMC is recently practiced due to its CO₂ utilization potential mentioned in Table 2, but appropriate catalyst selection is a critical issue. Carbamates have found wide range of applications, for example, in the production of urea, polyurethane plastics, cosmetics, and so on. From the statistics presented in Table 2, it is evident that the conversion of CO₂ to carbamates is currently not a well-established process and further advancement of catalyst and improvement of the overall process is required.

Algae are emerging as one of the sustainable sources of biomass, food, fuel, and other products.⁷² They can also be used for water purification. They absorb CO₂ and converts it into oxygen.⁷³ Algae production as energy crop has the potential to provide fuel for transportation.⁷⁴ It is obvious (from the statistics presented in Table 2) that the production of microalgae has significant potential for future CO₂ mitigation and biofuels production; however, production of microalgae in reactors is an emerging field for researchers. Biodiesel from microalgae has the potential to replace fossil fuels to a great extent in future, provided the economic feasibility is achieved.

Some of the chemical utilization processes like production of urea, methanol, salicylic acid, polyurethane, and polycarbonates from CO₂ are mature technologies while some are under development such as production of ethylene carbonate, propylene carbonate, ethane, and so forth and some processes like production of formaldehyde and acrylic acid are at the very initial phase of their development. Selection of chemical utilization process is a critical decision as the main aim of such processes is to ensure economic feasibility as well as environmental protection. LCA and process optimization play a critical role in this regard. The next section of this article presents the PSE prospective in optimal selection and improvement of the CO₂ conversion processes using various computational techniques and tools.

3 | PROCESS SYSTEMS ENGINEERING PERSPECTIVES

The use of various computational techniques and tools for the identification, analysis, design, and optimization of raw material conversion to useful products is becoming very important due to global competition and

strict regulations. Multiple tools and algorithms are developed in this regard for different applications. PSE has found wide applications in research and development as well as in industrial sector, starting from molecular level simulations to enterprise-level management and optimization. Main application areas of PSE are summarized in Figure 3. In this section, the role and prospective of PSE is presented in identifying reaction pathways and affinity of CO₂ capture and conversion with new materials; improving the operating conditions and equipment geometry/design; developing and analyzing the process and its economic as well as environmental impacts; and finally identifying the suitable conversion pathways by optimally selecting the most suitable option among the various available CO₂ utilization options. Though carbon capture is a well-developed process, but high cost associated with it is a major issue and many researchers are working to improve its economic feasibility. Since most of the situations involved carbon capture process integrated with CO₂ conversion, therefore, this section also touches the carbon capture processes. In this context, the discussion linked with molecular level simulations and CFD also includes carbon capture process. However, the major focus of this paper as well as this section is the utilization of CO₂. Further details on the current role of PSE and its future prospective in CO₂ utilization such as molecular level simulations, CFD, LCA, process-level simulations, and process optimization, are presented in the following subsections.

The overall framework that can be used to assess CO₂ utilization processes using computational techniques at various system levels is presented in Figure 4. In this

multiscale framework, molecular level simulations are the first step which requires the information regarding shape of the molecules involved in the process, force fields under which the system is operated, the process conditions and constraints. Results of these simulations yield the molecular interactions, molecular mechanics, and interfacial mechanics. These simulations can also harvest information about the transport mechanisms involved in the system. The results of the molecular level simulations, along with experimental data in the form of empirical relations could be used as an input for the CFD-level simulations which could yield the information regarding the process parameters, predicts the process performance, structurally analyze the process, and can give an information regarding the net CO₂ balance of the system under consideration. CFD results could then be used for the LCA studies which classifies the processes in terms of their GHG emission potentials. The processes giving net negative GHG emissions are techno-economically analyzed using process-level modeling and simulations and those giving positive emissions are either replaced with the other processes giving same product (process replacement) or the final product is changed with some other product performing the same function (product replacement). The thermodynamic and economic feasibility of CO₂ utilization processes is established from the information generated from process-level simulations. The thermodynamically and economically feasible processes are then ready for implementation while the infeasible processes are then optimized using process optimization techniques. The process will be implemented only if the process optimization is able to improve the thermodynamic and

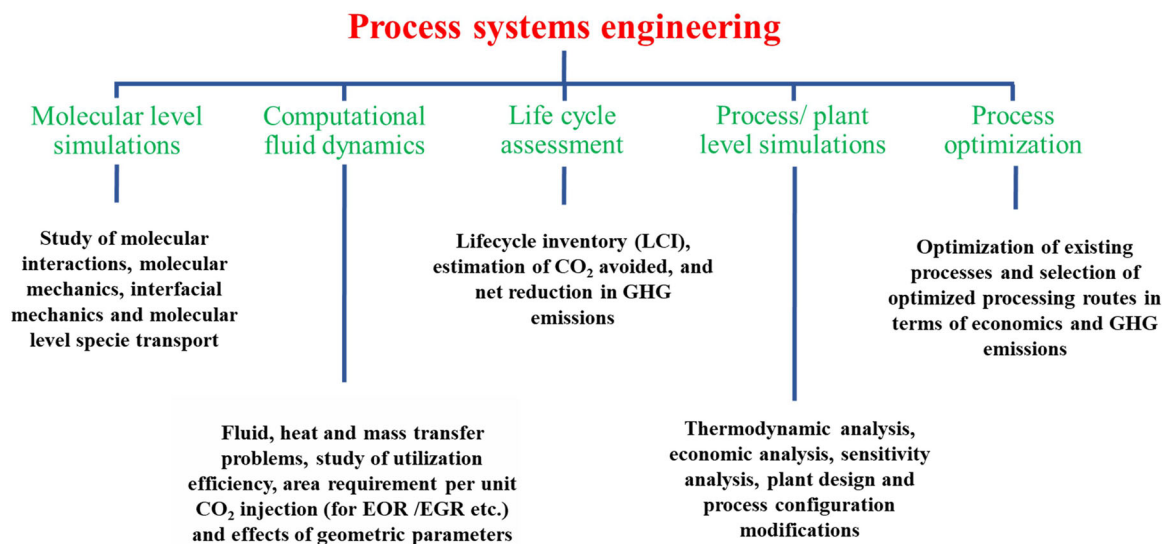


FIGURE 3 Use of PSE in development of CO₂ utilization processes

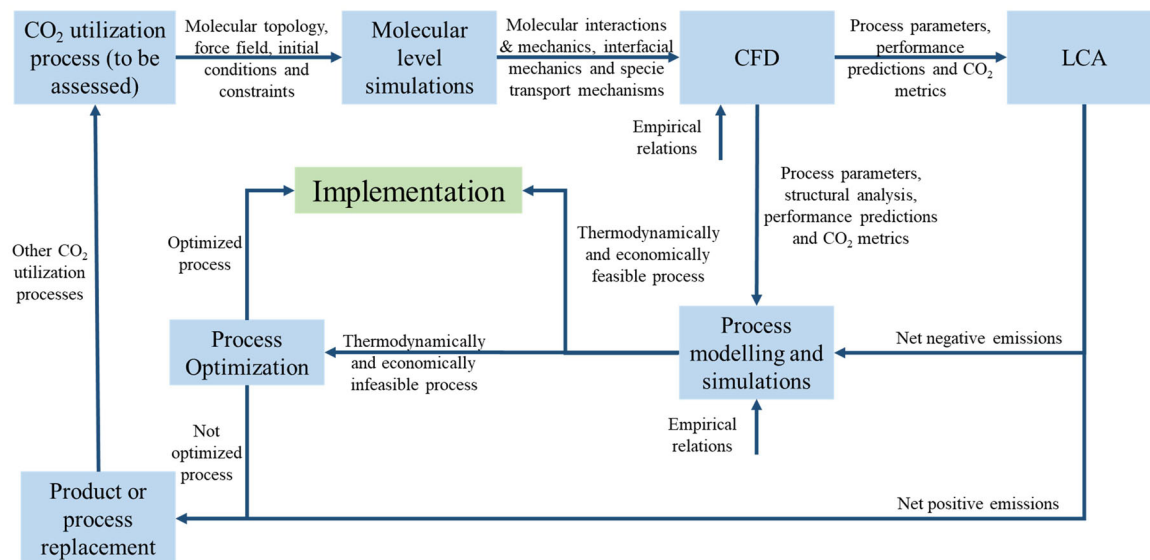


FIGURE 4 Framework to assess CO₂ utilization processes using PSE tools and techniques

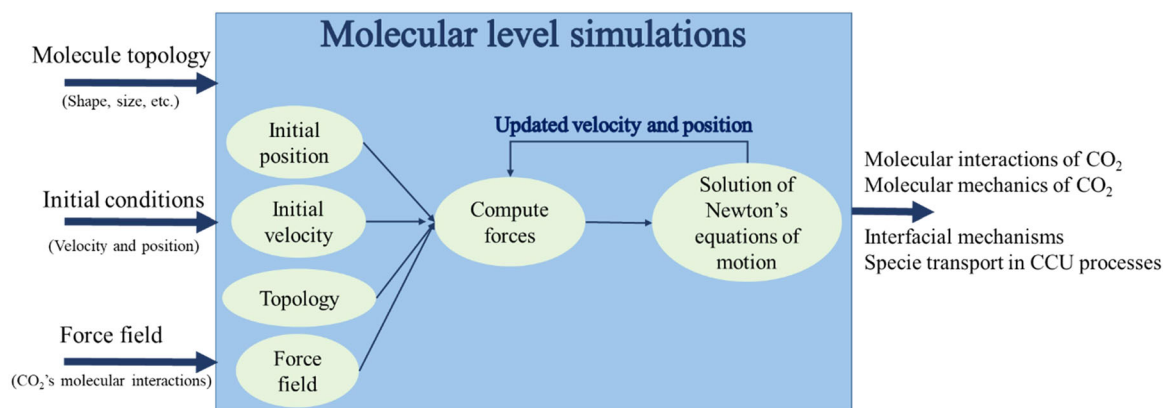


FIGURE 5 Schematics of a molecular level study

economic feasibility to an acceptable level, otherwise the process/product will be replaced (process replacement or product replacement).

3.1 | Molecular-level simulations

High computational speed is required for molecular level simulations.⁷⁵ Limited number of articles are available on carbon capture,^{76–80} physical utilization,^{81–86} and chemical utilization processes^{87–92} for identification of molecular interactions, study of diffusion such as adsorption capacity and selectivity of CO₂ in a given material, and estimation of activation energy. Schematics of a typical molecular level study is presented in Figure 5. A brief review of these studies is presented in the following paragraphs (and is summarized in Table 3) as

this information may be useful for the researchers and may be the initial step for this type of simulations to explore more CO₂ utilization processes, especially for chemical utilization.

In molecular dynamic (MD) studies, atoms and molecules are allowed to interact for a fixed period of time (to avoid steady state) to get insights about dynamic evolution of the system. Classical MD simulations were used to study the interactions between CO₂ and H₂O at ionic liquid (IL) interface.⁷⁶ The existence of a strong interaction between C2(+) and O(–) sites in ILs was observed. Diffusive dynamics were not significantly affected by the presence of CO₂, but presence of water hindered the diffusion of both CO₂ and IL. The molecular interactions associated with incorporation of CO₂ in montmorillonite clay using MD simulations were studied⁷⁷ and results showed a good match with

TABLE 3 Molecular level studies on carbon capture and utilization processes

Sr. #	Utilization/ Sequestration/ Capture	Process	Performance parameter	Parameters studied	Software used	Validation	Reference
1	Capture	Absorption	Diffusive dynamics of CO ₂	CO ₂ capture and effect of water on IL-CO ₂ mixture	LAMMPS MD	n/a	[76]
2	Capture	Intercalation (adsorption)	Evaluation of intercalation mechanism at molecular level	Behavior and structural analysis of CO ₂ in gas, liquid and supercritical state; montmorillonite and CO ₂ -intercladded montmorillonite	Gaussian 03 software	Yes (experimental)	[77]
3	Capture	Absorption	Investigation of zwitterion formation	Effect of hydrogen bond capacity of solvents on CO ₂ capture	Amber 12	n/a	[78]
4	Sequestration	EOR	Probing and design of CO ₂ EOR process	Contact angle, meniscus, injection rate, and interfacial width	LAMMPS	n/a	[81]
5	Sequestration	EOR	Oil displacement by CO ₂ /N ₂ slug flooding	Comparison of slug flooding with continuous injection processes	LAMMPS	n/a	[82]
6	Sequestration	EOR	Physics of CO ₂ injection for EOR	Hydrocarbon phase behavior and miscibility of CO ₂	LAMMPS	n/a	[83]
7	Sequestration	EGR	Kerogen volume change	CO ₂ and methane adsorption	LAMMPS	n/a	[84]
8	Sequestration	EGR	CO ₂ sorption	Nanopore size, average molecular weight of gas, pressure and temperature	TOWHEE	Yes (molecular density functional theory)	[85]
9	Sequestration	EGR	CO ₂ sorption capacity	Various clay minerals	MUSIC	n/a	[86]
10	Capture	Adsorption	Effect of nitrogen doping on selectivity of CO ₂ adsorption	Nitrogen doping	Gaussian 03 suite of programs	n/a	[79]
11	Capture	Adsorption	Adsorption characteristics of CO ₂	Induced polarity	VASP	n/a	[80]
12	Utilization	Methanol production	Activity, selectivity and stability of Cu/TiO ₂ and Cu/ZrO ₂ catalysts	Reaction mechanism of CO ₂ hydrogenation to methanol	VASP	Yes (compared with in situ experiments)	[87]
13	Utilization	Methanol production	Cu dispersion, its electronic state and polymorphic phases of ZrO ₂	Catalytic activity of Cu/ZrO ₂ catalyst in CH ₃ OH synthesis from CO ₂	VASP	n/a	[88]

TABLE 3 (Continued)

Utilization/ Sequestration/ Capture	Sr. #	Process	Performance parameter	Parameters studied	Software used	Validation	Reference
Utilization	14	Methanol production	Reaction mechanisms, effect of dopants (Cu, Pd, Pt, Rh) on kinetic performance of Ni(111) catalyst	Kinetic performance of clean Ni(111) and Ni(111)-M (M = Cu, Pd, Pt, Rh) catalysts	Quantum Espresso package	n/a	[89]
Utilization	15	Formic acid production	Energetics of H addition to CO ₂ , role of surface and subsurface H on formic acid production	Catalytic performance of Ni(110) catalyst for formate, carboxyl and formic acid production	VASP	n/a	[90]
Utilization	16	Hydrogenation of CO ₂	CO ₂ adsorption, dissociation and hydrogenation over Fe facets (100), (110), (111) and (211)	Catalytic properties of different Fe facets in hydrogenation of CO ₂	VASP	n/a	[91]
Utilization	17	Hydrogenation of CO ₂	Catalytic performance of RWGS reaction, CO ₂ conversion and CO selectivity	Catalytic behavior of metal catalysts (Pd, Ni, Cu, and Ag) in RWGS reaction	VASP	n/a	[92]

experimental and theoretical data. In another dynamic study,⁷⁸ the role of hydrogen bond in reactions of CO₂ with amines was investigated. Quantum and molecular mechanics (QM/MM) simulations were performed using the method of umbrella-sampling⁹³ using Amber 12 software for activation free energy identification of zwitterion ion formation. Ab initio molecular dynamic (AIMD) simulations were also carried out to confirm the results of QM/MM simulations.

Nonequilibrium MD simulations were carried out to investigate the adsorption of supercritical CO₂ and translocation of hydrocarbons in shale inorganic nanopores.⁸¹ Low CO₂ injection rate accompanying large injection volume showed amplification in oil recovery. In another study, CO₂/N₂ slug injection for EOR was investigated using MD simulations.⁸² CO₂'s swelling effect and N₂'s propelling effects were identified to be the key parameters for oil extraction. Slug flooding proved to be more effective in terms of displacement efficiency than continuous injection of CO₂, N₂ and flue gas, separately. In another study, phase behavior of CO₂ EOR was simulated using MD simulations⁸³ and reported high affinity of CO₂ molecule (to be adsorbed to the kerogen walls) than hydrocarbon molecule, resulting in displacement of hydrocarbon molecule, subsequently increasing the oil recovery.

Grand canonical Monte Carlo (GCMC) simulations were performed to validate the molecular density functional theory by simulating the EGR process.⁸⁵ Negative impact of the water presence was found for CO₂ adsorption. However, in case of CO₂ mixed with methane, the adsorption of CO₂ dominated in the presence of water. Competitive adsorption behavior of CO₂/CH₄ mixtures on various clay minerals was studied, in relation to EGR, using GCMC molecular simulations.⁸⁶ Results demonstrated the sorption capacity in clay materials to be of order montmorillonite > illite > kaolinite. Kerogen, CH₄, and CO₂ system was examined using MD simulations.⁸⁴ Swelling of kerogen was observed on sorption of CO₂ and CH₄; however, swelling caused by CO₂ was less intense than that caused by CH₄. This would lead to an increase in recovery of gas from shale. Moreover, CO₂ was observed to be strongly bound to kerogen as compared to CH₄ providing a mean to sequester its large volumes.

Molecular level studies can also be used to estimate the adsorption capacity of CO₂ on different surfaces. The selective adsorption of CO₂ from N₂ by nitrogen doping of mesoporous carbon using molecular simulations exhibited the increased adsorption capacity of mesoporous carbon (from 3 to 12 mmol/g) at 1 bar and 298 K.⁷⁹ The effect of surfaces, containing oxygen, on adsorption of mixtures including CO₂/H₂O, CO₂/CH₄ and CO₂/N₂

using molecular simulations were presented.⁸⁰ Polarity was induced in the surface which increased the selectivity of CO₂ over CH₄ from 2 to greater than 5 and the selectivity of CO₂ over N₂ was increased from 5 to 20. However, selectivity of H₂O was greater than CO₂ in carbon-based system containing hydrogen.

As already discussed, most of the reactions of CO₂ are carried over catalysts. Interaction of CO₂ with catalyst surfaces and mechanism of CO₂ conversion can be studied on micro scale using the molecular level studies. Reaction mechanism of CO₂ hydrogenation to CH₃OH using Cu/TiO₂ and Cu/ZrO₂ catalysts was studied on molecular level by combining density functional theory (DFT) and kinetic Monte Carlo (KMC) simulations with in-situ experimental measurements.⁸⁷ ZrO₂ was found to be more effective than TiO₂ in terms of both catalyst activity (synergy between reduced Zr³⁺ and Cu sites) and CH₃OH selectivity (for 100 ml/min solution flowrate, 28.3% in case of ZrO₂ and 19.1% for TiO₂). In another study, activity of Cu/ZrO₂ catalyst in CH₃OH synthesis from CO₂ was studied using quantum chemical calculations.⁸⁸ Conditions of catalyst preparation significantly impacted the Cu dispersion, its electronic state and polymorphic phases of ZrO₂ (tetragonal and monoclinic phases). Catalytic activity for CH₃OH synthesis increased with increasing t-ZrO₂ (tetragonal phase) content.

DFT and microkinetic studies were used to investigate the CO₂ hydrogenation to methanol on clean Ni (111) and Ni(111)-M (M = Cu, Pd, Pt, Rh) surfaces.⁸⁹ Formate mediated (HCOOH*) and carboxyl mediated (HCO*) routes were identified to be the main pathways for methanol production. Cu, Pd, and Pt dopants successfully increased the kinetic performance of Ni (111) surface in formate mediated route while in case of carboxyl mediated route, kinetic performance was found to be increased in case of Cu, Pt, and Rh doping. A plane-wave DFT study of CO₂ hydrogenation to formate, carboxyl, and formic acid on Ni(110) was carried out.⁹⁰ It was presented that CO₂ could be hydrogenated to formate in the presence of surface H. However, this surface H hindered the further hydrogenation of formate to formic acid. Emerging of the subsurface H was suggested to overcome the barrier in formate to formic acid production. It was concluded that hydrogenation of CO₂ to formic acid could take place on Ni(110) catalyst only in the presence of subsurface H.

Investigations of facets effect on CO₂ adsorption, dissociation and hydrogenation over Fe catalysts were performed.⁹¹ Fe facets played an important role in formation of key intermediates and hence, changed the preferred CO₂ conversion pathway. CO₂ adsorption on Fe (211) and Fe (111) was found to be stronger than other facets. Fe (111) favored the associative pathway (HCOO*

formation) while Fe (100) and Fe (110) facets were more selective toward CO* formation. Fe (211) exhibited a competitive preference toward CO* and HCOO*. In another study, catalytic behavior of metal catalysts (Pd, Ni, Cu, and Ag) was investigated in high temperature reverse water gas shift (RWGS) reaction using in-situ surface analysis and DFT calculations.⁹² Results presented that Cu, Pd and Ni catalysts favored the H adsorption while Ag surface was found to be unfavorable.

Currently, carbon capture by absorption in amine-based solvents is a well-developed process; however, it consumes substantial amount of energy for the regeneration of the solvent. Study of solvent-CO₂ interactions on molecular level may help identifying the suitable solvent for CO₂ capture for a specific case. The suitability of the solvent may vary for each system as solvent performance and economics depends upon several factors including the flue gas composition, CO₂ purity required, price of solvent and characteristics of the solvent used. Moreover, in the case of EOR and EGR, molecular level studies could identify the mechanisms that can increase the CO₂ sequestration, simultaneously increasing the production of fuels. Molecular-level investigations can give insights to chemical utilization processes of CO₂. Limiting mechanisms, barriers and molecular interactions in CO₂ conversion processes could be evaluated by studying these systems at micro scale. However, this computational technique has just emerged, and its applications are quite rare. One of the major obstacles in studying CO₂ utilization processes at molecular level is the high computational power requirement. This obstacle could be crossed by successfully implementing the Paris accord which vowed finance flows in minimizing CO₂ emissions.

3.2 | CFD

CFD considers continuum level simulations to solve partial differential equations (PDEs). Mass, momentum, and energy balance equations on small fluid elements are discretized and solved using numerical methods.⁹⁴ CFD studies for CO₂ utilization are limited and most of the available literature covers carbon capture.⁹⁵⁻¹⁰⁰ A few CFD studies are available on CO₂ utilization processes.¹⁰¹⁻¹⁰⁹ A brief summary of literature in this regard is presented in Table 4. CFD simulations can be used to carry out the sensitivity analysis of the processes, that is, to evaluate the effect of various parameters (e.g., ratio of liquid to gas flows, pressure, temperature, steam flows, etc.) on energy penalty, absorption efficiencies, reactor performance, or other performance indicators of specific process. Schematics of a typical CFD study is presented in Figure 6.

TABLE 4 CFD studies on CO₂ utilization

Sr. #	Utilization/ Sequestration/capture	Process	Performance parameter	Parameters studied	Software used	Reference
1	Capture	CLC	CLC performance	Effect of particle size, flowrate of gas and temperature of bed	ANSYS FLUENT	[95]
2	Capture	Amine based PCCC	Capture efficiency of packed bed column	System hydrodynamics	ANSYS FLUENT	[96]
3	Capture	Solid sorbent carbon capture	Reactor performance	Gas flow, solids circulation rate and heat transfer	CPFD's BARRACUDA code	[97]
4	Capture	Solid sorbent regeneration	Design of regenerator of solid sorption carbon capture process	Pressure, solid circulation rate and gas velocity	ANSYS FLUENT	[98]
5	Capture	Solid sorbent carbon capture	Hydrodynamics and adsorption of CO ₂ in the reactor	Cut cell mesh, modeling method and assessment of CFD tools	FLUENT and BARRACUDA	[99]
6	Capture	Oxy-coal combustion	Feasibility of converting conventional power plant to oxy fired	Oxygen concentration, recycle ratio, excess oxygen, coal & gas mass flow rates	ANSYS FLUENT	[100]
7	Sequestration	EGR	CO ₂ storage feasibility	CO ₂ injectivity, storage capacity, CO ₂ trapping of EGR, methane production	GEM	[101]
8	Sequestration	EGR	Economic feasibility and sequestered CO ₂	CO ₂ cost, ratio of CO ₂ injection to increase in methane production, natural gas price	Tempest	[102]
9	Sequestration	EOR	Simulator performance and oil recovery	Primary, secondary and tertiary stages of production and CO ₂ sequestration	STOMP-EOR	[103]
10	Sequestration	EOR	Oil recovery factor	CO ₂ injection rate and injection pressure	COZView/COZSim	[104]
11	Sequestration	EGS	Mass flow and heat extraction rates	Working fluid (CO ₂ /H ₂ O) and gravity effects	TOUGH2	[105]
12	Utilization	CO ₂ methanation	Pressure drop, temperature distribution	Spatial variations	OpenFOAM	[106]
13	Utilization	H ₂ production	Temperature and concentration profiles both radially and axially	Radial distance between center of reactor and center of membrane, H ₂ flux	COMSOL Multiphysics®	[107]
14	Utilization	CO ₂ reforming of CH ₄	Analysis of membrane reactor for CO ₂ reforming of CH ₄	Hydrogen permeation phenomenon, effect of RWGS reaction and reactor configuration	COMSOL Multiphysics®	[108]
15	Utilization	Methanol production	Coupling of Molecular level study with CFD for reactor optimization	Reaction mechanism, surface kinetics, CO ₂ conversion and methanol selectivity	Macros 2.0 and OpenFoam	[109]

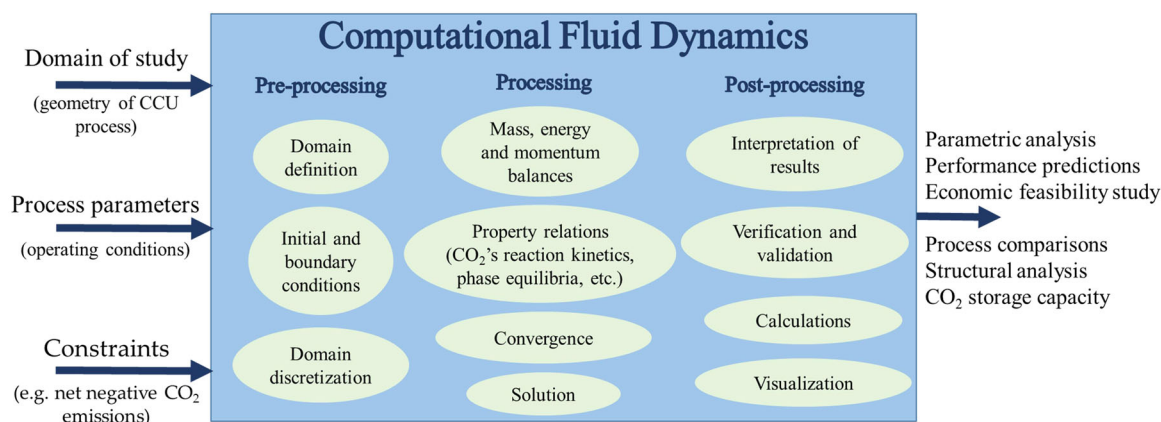


FIGURE 6 Schematics of a computational fluid dynamics study

The model of a chemical looping combustion (CLC) fuel reactor to find the optimal operating conditions was developed⁹⁵ using Fluent. High temperature of the bed, low flow rate of the gas and smaller particles resulted in enhanced performance of CLC. A post combustion carbon capture (PCCC)-based packed bed absorption system was simulated using amine solvent.⁹⁶ Two fluid Eulerian model was used to study the detailed hydrodynamics. Absorption efficiency was found to be sensitive to the ratio of liquid to gas mass fluxes. The model proved to be reliable because of its consistency with experimental data. The model of lower riser of solid sorbent CO₂ reactor using CFPD's BARRACUDA code exhibited the improvement of the reactor performance with increased flow rate of solids.⁹⁷ Reactor performance was also found to be the function of molar sorbent to CO₂ ratio entering the reactor. The three-dimensional simulations of regeneration unit of carbon capture process was performed using MgO-based solid sorbents.⁹⁸ It was concluded that back mixing could be avoided using high regenerator pressure, high gas velocities, and more solid flow. Moreover, high steam velocity was responsible to dilute the CO₂ concentration of the system, thus increasing the regeneration efficiency.

A low temperature PCCC reactor was investigated by CFD simulations using both FLUENT and BARRACUDA to compare the strengths and weaknesses of these CFD tools.⁹⁹ The reactor was silica supported amine-based fluidized bed reactor. FLUENT simulations were found to be unstable for given reactor conditions while BARRACUDA simulations were found stable under appropriate simplifying assumptions. An integrated simulation of power plant with capture plant was carried out in which a detailed CFD model was used to study the gas phase combustion as well as radiative heat transfer from furnace walls and re-boiler.¹⁰⁰ The resultant insights were used to suggest the modifications in the

heat transfer components. These modifications were then implemented in the gPROMS (a process modeling tool) to accommodate the effect of different gas compositions.

Physical utilization processes were assessed for their CO₂ sequestration potential, economic feasibility, and process effectiveness. CO₂ storage facility in New Albany shale using EGR was investigated.¹⁰¹ The well was simulated using GEM simulator. Impacts of CO₂ injection, storage capacity, and effectiveness of EGR system were studied. The well was found to have the capacity to accommodate 4×10^4 metric tons of CO₂, injected within 5 years. In another study, a natural gas reservoir using CO₂ as working fluid for EGR was simulated¹⁰² using a 3D model. The results showed an increased gas recovery along with sequestration of large volume of CO₂. A simulation tool was developed to simulate CO₂ injection in the western section of Farnsworth Unit, Texas¹⁰³ using a model composed of balance equations, equation of state and phase relationships. Furthermore, the heterogeneities in the phases were modeled using fluid equilibria with injected CO₂. These simulations could help in understanding the mechanisms of CO₂ utilization and its ultimate fate in petroleum reserves. In another study, EOR from depleted oil reserves was simulated using multiphase flow solver package COZView (provide GUI for pre- and post-processing)/COZSim (simulator).¹⁰⁴ The simulation resulted in increased oil recovery along with more efficient utilization of CO₂. This study could be applied to other similar systems, for example, EGS, EGR and enhanced water recovery. Numerical simulations of CO₂ and water injection for EGS were carried out¹⁰⁵ and substantially higher heat extraction was found for CO₂ as compared to water. A steady-state solver was developed to study reactions and heat transfer of CO₂ methanation process.¹⁰⁶ This solver could be used to capture the thermal hot spots as well as to predict the carbon conversion while maintaining the heat transfer in

the reactor with great accuracy. Moreover, it could also be used for modeling the CO₂ methanation process.

CO₂ reforming of methane was analyzed, using 3D CFD study, in a packed-bed reactor and a membrane reactor.¹⁰⁷ Heating tube as a heat source was used at the center of the reactor. Temperature and concentration profiles were visualized both axially and radially. H₂ enhancement was found to be proportional to radial distance between center of the reactor and center of the membrane. A 2D CFD model of catalytic membrane reactor (for dry reforming of CH₄) was developed to visualize the reaction and hydrogen permeation phenomena.¹⁰⁸ The membrane with high hydrogen permeance inhibited the RWGS reaction thus reducing the steam yield and increasing the yield of hydrogen. The study concluded that the most crucial parameter for membrane reactor design is the hydrogen flux permeation profile. In another study, molecular level simulations were coupled with CFD study to investigate the CO₂ hydrogenation to CH₃OH over Cu/ZnO/Al₂O₃ heterogeneous catalyst.¹⁰⁹ Molecular-level study was aimed at obtaining the insights to the upper most layer conditions during reaction while CFD was focused at nonuniform catalytic reduction of CO₂ to formate. This coupled model proved to be fruitful in optimization of the catalytic reactors.

Using CFD analysis, the performance of cost intensive carbon capture and utilization processes could be analyzed to identify the challenging mechanisms and optimal operating conditions. These studies could also be used to estimate CO₂ storage capacities of EOR and EGR wells. CFD studies are a decent tool to model CO₂ utilization processes with the aim of process improvement. Although these studies can provide useful information about processes, results of these studies are never exact (discretization errors, approximation errors, round off errors, and convergence errors). Moreover, involvement of chemical reactions (chemical CO₂ utilization) in CFD models complicates the problem to a great degree. However, these issues could be resolved by using smaller grids, least error tolerances, higher order discretization, and no doubt a high speed computer.

3.3 | LCA

LCA refers to the study of environmental impacts of products and resources used all the way through product's lifecycle, starting from raw material acquisition, moving toward production, then utilization and ending up in waste management (as presented in Figure 7).¹¹¹ Following are the four phases of LCA¹¹²: (1) goal and scope, (2) inventory analysis, (3) impact

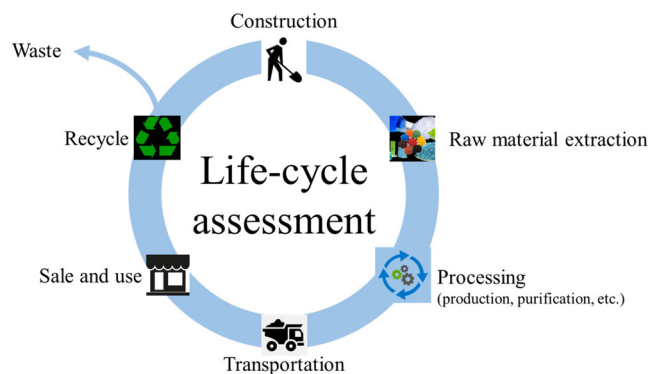


FIGURE 7 Stages of a typical LCA study. Source: Modified from Brusseau,¹¹⁰ with permission from publisher.

assessment, and (4) interpretation. Selection of CO₂ utilization processes is a critical decision. One of the important questions that must be addressed while CO₂ utilization process selection is “whether or not the process will give net reduction in GHG emissions?”. Reduction in environmental impacts by implementation of CO₂ utilization processes cannot be taken for granted and the environmental feasibility should be evaluated. LCA is the broadly accepted way to assess CO₂ utilization processes among industrialists and researchers.¹¹³ However, LCA studies on CO₂ utilization processes are limited to a few processes only, including production of DMC, methanol, polymers, formic acid, carbon monoxide, methane, and MgCO₃.

The CO₂ footprints of mineral carbonation (MgCO₃ production) were evaluated by considering four projected scenarios.¹¹⁴ In the first two scenarios, CO₂ was captured from natural gas combined cycle (NGCC) power plant by amine-based PCCC and in other two scenarios direct mineralization of CO₂ was employed. Ecoinvent and GaBi life cycle engineering packages were used for analysis and the two scenarios with direct CO₂ mineralization were found to be superior in terms of CO₂ avoided. In another study, a coal-fired power plant with utilization of captured CO₂ to MgCO₃ was assessed using Aspen Plus[®] and Sima Pro[®]¹¹⁵ and mineralization of 1 ton CO₂ resulted in 483 kg CO₂ avoided. The conventional route (from phosgene) and CO₂-based route of DMC production were compared using environmental LCA.¹¹⁶ Process impacts on the greenhouse effect, ozone layer, nitrification, acidification, and photochemical oxidant formation were evaluated. Urea route (CO₂ based) for DMC production demonstrated low impacts on the environment.

A framework to environmentally assess CCU processes using LCA was developed in which CO₂ was captured directly from the atmosphere as well as from coal-fired power plant (CFPP).¹¹⁷ The captured gas was

utilized for methanol and polymer synthesis. The CCU process resulted in 59% reduced GHG emissions for methanol. Whereas CCU process for polymer production resulted in slightly higher global warming potential due to increased emissions during plant construction. The reduction in global warming potential, when conventional processes are replaced by CO₂-based processes for the production of formic acid, CO, methanol, and methane, was investigated.¹¹⁸ The formic acid production presented maximum emission reduction followed by CO and methanol while methane production presented lowest emission reductions. In another study, formic acid production by electrochemical reduction of CO₂ was analyzed.¹¹⁹ The results were compared with conventional formic acid production and CCS route. The CCS route provided more reduction in CO₂ emissions as compared to CCU route while CCU proved to be more efficient in terms of economics and fossil fuel consumption. In another work, it was concluded that CO₂-based production of formic acid reduced climate change impact and fossil fuel depletion by 53.6% and 28.3%, respectively.¹²⁰

LCA of EOR process was performed using PCCC from a combined cycle power plant.¹²¹ The results showed 80% decrease in CO₂ emissions from the power plant when captured CO₂ was used for EOR. In another study, net lifecycle CO₂ emissions from EOR process were investigated.¹²² It was found that for 1 ton of CO₂ sequestered, 3.7–4.7 tons of CO₂ were released. Several studies^{123–127} are available on LCA of CO₂ utilization for microalgae growth using different functional units and different capture technologies. Further details including scope of LCA, software used, capture technique employed, utilization process assessed, functional unit used and findings are summarized in Table 5. LCA studies are very important to evaluate the environmental feasibility of a CCU process. Usually this is the first step in selection of CCU process; however, LCA results are highly uncertain because of involvement of if-then scenarios. Moreover, definition of scope of LCA studies is also a critical decision as estimation of emissions from transportation of raw material or products has uncertainties associated with it; however, this issue can be resolved by development of precise correlations or using real-life process data. To get maximum benefit from these studies, integration of LCA with techno-economic analysis of the CO₂ utilization processes was proposed¹²⁸ but their integration methods are still to be developed. Methodological choices (e.g., boundaries of the system, allocation methods, technology level, and marginal/average data) were identified to be the major sources of uncertainty and this type of uncertainty can be avoided by agreeing upon a standardized framework on how to do LCA studies.¹²⁹

3.4 | Process/plant-level simulation

Process-level simulations are employed for process development, process design, cost estimation, process optimization, process modification, and process operation control, and so on. Schematics of a general process and plant-level simulations is presented in Figure 8. This section presents process-level simulations of the CO₂ utilization processes or plants including various levels of the process systems such as a single unit, a plant or an integrated system. The main objectives include the performance prediction and performance improvement in terms of productivity and quality of the product by considering both the economic and environmental factors. Various software packages are used for this purpose including AspenOne (Aspen HYSYS, Aspen Plus, etc.), CHEMCAD, DWSIM, Pro/II, TRNSYS, and so forth. In this context, substantial literature for CO₂ capture is available but the main focus of this section will be on CO₂ utilization. This section is divided into two subsections: (1) a very brief summary of process simulations-related contributions to CO₂ capture, (2) a critical review of process-level simulations for CO₂ utilization.

3.4.1 | Carbon capture

Literature on modeling and simulation of carbon capture processes is vastly available which includes custom-based process models and flow sheet type simulation models. The objectives of this type of modeling and simulations include model validation against a pilot plant data or commercial plant,^{130,131} parametric studies,^{132,133} process design,¹³⁴ energy and economic analysis,^{135,136} process modifications,^{137,138} use of mixed solvents,^{139,140} process integration,¹⁴¹ flexible operation^{142–144} and advanced strategies for online control and optimization.^{145,146} The details of the above citations are not presented as carbon capture is not the main focus of this review. The aim of this section is to keep the readers aware of main contributions of process-level simulations regarding carbon capture which is an important part of CCU.

In the above cited literature, various authors have contributed in reducing the economic burden by analyzing the selection of suitable capture process (absorption, adsorption, membranes, etc.), selection of suitable solvent (chemical, physical, mixed, etc.)/material (as sorbents and membranes), selection of optimal operating conditions (temperature, pressure, solvent loadings, etc.), development of improved process designs (single column vs. double column, plate column vs. packed column, temperature swing vs. pressure swing, etc.), process

TABLE 5 Life cycle assessment of CCU processes

Sr. #	LCA Scope	Software used	Capture technique	Utilization/Sequestration process	Functional unit	Conclusions	Reference
1	Mining, crushing & transportation of ore, CO ₂ recovery & sequestration	Ecoinvent and GaBi life cycle engineering	Amine based PCCC & direct carbonation from flue gas	MgCO ₃ production	1 MWh electricity production	Direct carbonation processes were better in terms of CO ₂ avoidance	[114]
2	CFPP, capture plant, coal & ore mining, transportation, carbonation	Aspen Plus [®] and Sima Pro [®]	MEA based PCCC	MgCO ₃ production	1 ton CO ₂ been sequestered	483 kg CO ₂ been avoided	[115]
3	Conventional and CO ₂ based DMC production processes	Eco-indicator '95	Carbon capture using MEA	DMC production	1 kg of DMC produced	CCU process was more environmental friendly	[116]
4	CO ₂ capture from the CFPP and by direct air capture; Production of methanol & polymer from CO ₂	Ecoinvent	PCCC using MEA; direct air capture	Methanol & polymer production	1 ton CH ₃ OH & 1,273 ton CO ₂ -eq/ton polym.	59% less emissions (CH ₃ O H); Higher global warming potential (polymer)	[117]
5	Conventional and CO ₂ based processes for specific product formation (use and end of life phases are neglected)	GaBi, ecoinvent and Co ₂ RRECT	Both flue gas of coal power plant and direct capture from air were considered	Formic acid, CO, methanol and methane	1 kg hydrogen consumed	Reduction in global warming potential were in order: Formic acid > CO > methanol > methane	[118]
6	Both CCU and CCS processes	GaBi, ecoinvent & TIAM-UCL	PCCC	Formic acid production	1 kg of formic acid by each plant	Economics of CCU & emissions for CCS were better	[119]
7	Conventional and CO ₂ based formic acid production	SimaPro	PCCC	Formic acid production	1 kg of formic acid by each process	CO ₂ based process was environmentally feasible one	[120]
8	Power plant with carbon capture, compression, transport and EOR	Strømman and Solli's software	PCCC using amines	EOR	1 Sm ³ of oil recovered	Utilization by EOR resulted in 80% reduced emissions	[121]
9	Coal mining to combustion; CO ₂ capture to transportation; crude oil extraction to combustion	Suebsiri and McCoy's models	PCCC using Selexol	EOR	1 barrel of oil for energy analysis, entire project for emissions	EOR results in net positive CO ₂ emissions when whole lifecycle was assessed	[122]
10	Biodiesel production from microalgae in open pond and combustion of produced diesel	Ecoinvent	Direct utilization of CO ₂ from industrial sector	Biodiesel from microalgae	1 MJ of fuel	Some improvements were suggested to make biodiesel environmental friendly	[123]

(Continues)

TABLE 5 (Continued)

Sr. #	LCA Scope	Software used	Capture technique	Utilization/Sequestration process	Functional unit	Conclusions	Reference
11	Biodiesel from microalgae with canola & ultra-low sulfur diesel	SimaPro 7	PCCC	Biodiesel	Tonne-kilometer	Biodiesel resulted in less GHG emissions	[124]
12	Biodiesel production from microalgae by various methods	Ecoinvent, CED & BEES	Direct flue gas injection	Biodiesel	10 GJ biodiesel	86% reduction in emissions compared to base case	[125]
13	Biodiesel production from microalgae in an open pond	Microsoft Excel, crystal ball	Flue gas injection and 100% CO ₂	Biodiesel	Vehicle kilometers traveled (VKT)	Special focus on conversion & cultivation is needed	[126]
14	Biodiesel production from microalgae in open pond in flat plate PBR	BUWAL 250 and ecoinvent data v2.0	Direct utilization of flue gas from power plants	Biodiesel	8.94 × 10 ¹⁰ MJ of diesel fuel per year	A compromise between global warming and energy potential is needed	[127]

configuration and energy integration (integration of compressor intercooling with solvent regeneration, integration of shift reactor with capture process, capture plant integration with combined cycle, etc.) as well as advanced strategies of operation and control (capture level reduction and solvent storage mode of flexible operation, online optimization using model predictive control, self-optimizing control, etc.). Though carbon capture is a well-developed process, however, various efforts are in progress to reduce its economic impacts and further improvements are still required to implement this technology on commercial scale.

3.4.2 | Carbon dioxide utilization

The use of process modeling and simulation has wide application range as CO₂ utilization is gaining importance to mitigate climate change issues. Several researchers have simulated CO₂ utilization processes to assess their feasibility, environmental, and economic benefits. The discussion of this section can be broadly classified into following categories: thermodynamic analysis, environmental analysis, economic analysis, and plant design. Thermodynamic analysis refers to the study of reaction conditions, equilibria, models and process parameters. In environmental analysis, environmental emissions data and assessment of environmental impacts of process is involved. In economic analysis, evaluation of the economic parameters and economic consequences is the major aim. Combined economic and environmental analysis is known as sustainability analysis which is mostly the key analysis in selection of a CO₂ utilization process. Plant design analysis involves the detailed evaluation of equipment sizing, and process material and energy flows.

A number of CO₂ utilization processes have been thermodynamically analyzed by various authors. The effect of different operating conditions was evaluated for gasification of carbonaceous feedstock using CO₂ and a mixture of CO₂ with oxygen or steam.¹⁴⁷ Optimal operating temperature of 850°C was identified based on the minimum requirement of energy for complete carbon conversion. Less energy input was required for biomass as compared to coal. Use of cogasification agent such as steam or oxygen reduced the energy requirements but at the cost of reduced CO₂ conversion. The thermodynamic analysis of utilization of CO₂ from combined heat and power (CHP) system based on cogasification of coal and biomass was presented.¹⁴⁸ Optimal supply ratio of CO₂ (0.065) resulted in 0.64% and 0.18% increase in energy conversion efficiency and exergy efficiency, respectively. A study involving thermodynamic analysis of a CO₂

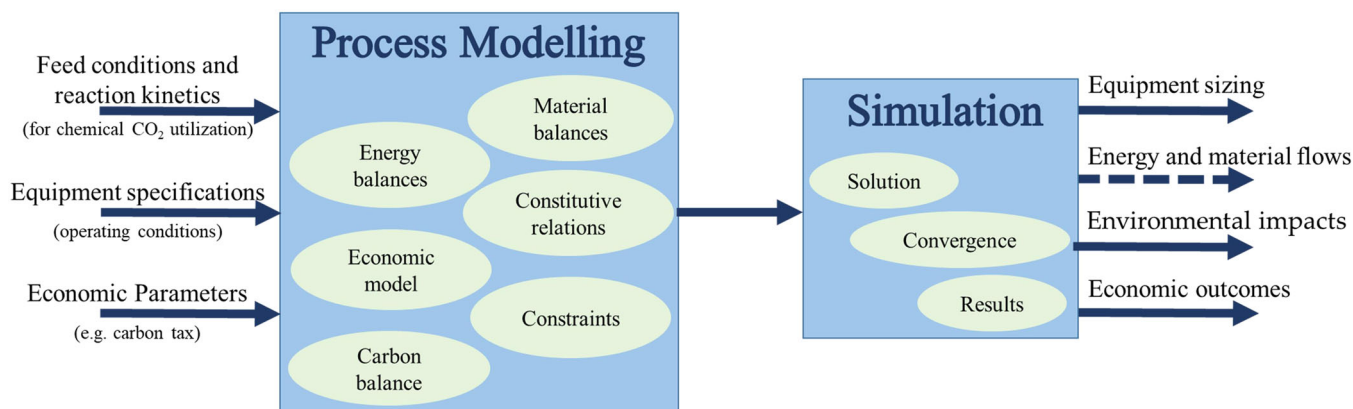


FIGURE 8 Schematics of process modeling and simulation studies

hydrogenation to methanol with in situ water sorption was carried out.¹⁴⁹ Within the optimal range of operating temperature (220–270°C) and pressure (50–70 bar), the yield of methanol was almost 130% higher in the current process compared to direct hydrogenation process. Continuous water removal shifted the thermodynamic equilibrium toward the completion of the reactions of CO₂. Furthermore, achievement of low recycle indicated the requirement of small size of the reactor and other auxiliary equipment's, leading to process intensification and hence reduced costs. ANOVA analysis of methanol synthesis process was used¹⁵⁰ to evaluate the optimal conditions of CO₂ hydrogenation. The use of membrane reactor without recycle, operating at 200°C and introduction of 10% CO in feed was suggested. The resulting CO₂ conversion and methanol yield were found to be more than 60% compared to conventional values of 33% and 27%, respectively. The steam-biomass reforming (SBR) process for conversion of CO₂ to syngas was investigated.¹⁵¹ Various raw material ratios (methane to CO₂ ratios of 2:3, 1:1 and 3:2), steam to carbon ratios of 1–2 and temperature range of 873–1123 K was considered.

Apart from thermodynamic analysis, process-level simulations are also used to analyze the CO₂ utilization processes from economics point of view. A process should be economically feasible for its implementation on industrial scale, and economic feasibility can be assessed using computational tools. The economic and thermodynamic analyses are integrated in most of the studies. This integration can assist the researchers to analyze the effect of various parameters on economics of overall process. Such analysis can help the selection of optimized process conditions. The economic feasibility of CO₂ utilization in pyrolysis of biomass for biofuel production was evaluated.¹⁵² Incorporation of subsidies and taxes in the economic analysis rendered the biofuel

cost-competitive to petroleum derived fuels. The use of two different software packages to carry out economic analysis of EGS was reviewed.¹⁵³ A newly developed software US GEOPHIRES can simulate the electricity production as well as heat output for direct use, and EURONAUT software can effectively study the effect of drilling depth on performance of whole process. A framework for economic analysis of EOR process was presented and two oil fields in Ohio were analyzed.¹⁵⁴ The reported framework comprised of three models: (1) reservoir model (CO₂ injection, oil production, and CO₂ production), (2) revenue model (net revenue, market price of oil, tax rate), and (3) cost model (total cost of installation, cost of pipelines, O&M cost, and CO₂ capture cost). This methodology can be used for initial screening of EOR projects as limited data are required for these models.

Techno-economic analysis of different CO₂ utilization routes for DMC production was performed.¹⁵⁵ Four routes of CO₂ utilization were considered namely: (1) direct synthesis route, (2) urea route, (3) propylene carbonate route, and (4) ethylene carbonate route. Ethylene carbonate route proved to be the best in terms of energy consumption, net CO₂ emissions, global warming potential, and human toxicity. The yield of DMC in these processes were of the order 4 > 2 > 3 > 1. The power to gas (PtG) technologies were assessed using a techno-economic analysis for utilization of CO₂ within coal-to-liquid facilities.¹⁵⁶ PtG was classified into two business models namely power-to-methane (PtM) and power-to-syngas (PtS), and three cases for each business model (PtS-Scenarios 1,2,3 and PtM-Scenarios 1,2,3) were developed depending upon CO₂ in feed (i.e., 10%, 20% and 50% of total CO₂ emissions, respectively). Only PtS scenarios 1 and 2 were economically competitive in current situation, and only PtM scenario 3 was not found to be feasible for future market. Thermo-economic

analysis of flexibly operating IGCC power plant in power only mode and multiproduct mode was carried out under varying methane, ammonia, and electricity prices.¹⁵⁷ It was found that total product value (sum of the selling value of all products, i.e., electricity, methane and ammonia) could be increased significantly by varying the production decisions against the variable market prices. Total product value was observed to be very sensitive to electricity price while ammonia price had the least effect on total product value.

A detailed thermo-economic analysis for the production of methanol from CO₂ and hydrogen was carried out¹⁵⁸ using Aspen Plus. Operating temperature and pressure of electrolyzer-based methanol plant were optimized using thermodynamic analysis. Economic analysis was performed based on the thermodynamic findings. Sensitivity analysis was used to find the minimum selling price of methanol for a payback period of 10 years using different electricity purchase prices. In spite of the increased energy consumption (at high pressure), the specific methanol production cost was reduced. The electrolyzer was the most critical component. However, the methanol production cost was 800 €/ton (almost twice its market price). To overcome this high cost, the sale of oxygen was proposed which could reduce the methanol cost by around 30%. In another study,¹⁸ methanol production by catalytic hydrogenation of CO₂ captured from cement plant was presented using thermo-economic analysis. The process was found to have the ability to treat 2475 ton CO₂/day but production of hydrogen was identified to be the main cost burden on overall economy. Integration of the environmental analysis with thermodynamic analysis can give insights to the overall carbon footprints of the process. In a similar study, methanol production process (by CO₂ hydrogenation) was integrated with solid oxide electrolysis (SOE) process.¹⁷ The energy integrations coupled with parametric analysis reduced the cost of methanol from 1063 \$/ton to 701.5 \$/ton. Techno-environmental analysis of CO₂ utilization for the production of DME via dry reforming of methane into syngas was performed using Aspen Plus and hybrid LCA.¹⁵⁹ Solvent-based CO₂ capture was employed to capture its emissions from a hydrogen production unit in a refinery. It was found that 94% of the total captured CO₂ been utilized for DME production and only 9% of CO₂ was avoided due to direct CO₂ formation during DME manufacturing and dry reforming process.

Plant design and modification is a major application area of process-level simulations. A mathematical model was used to simulate the methanol synthesis from CO₂ and H₂ in ceramic membrane reactor.¹⁶⁰ The results showed a good match with experimental data and

indicated increased methanol conversion and selectivity as compared to traditional reactor. A coproduction system producing electricity and DME was simulated.¹⁶¹ Gross and net electric outputs were 371.6 and 275.1 MW, respectively with 51.78 Mt/h yield of DME. The efficiency of the coal gasification-based coproduction plant was estimated to be 46.1% (significantly higher than its conventional counterpart). The conversion of CO₂ captured from industrial processes to urea and methanol was simulated²⁶ to produce 1600 ton/day of urea with purity level of 56% by weight and 1300 ton/day of methanol with purity level of 98% by weight. The process released 0.6 ton CO₂ per ton of CO₂ consumed (net negative CO₂ emissions) in case of urea and 6.8 ton CO₂ per ton of CO₂ consumed (net CO₂ emissions) in case of methanol production (when hydrogen is produced by using electricity from fossil fuels). In another study, a model of the methane reforming reactor for methanol production was presented and a tradeoff between maximum methanol production and maximum CO₂ abatement was identified.¹⁶²

Methanol production process by CO₂ hydrogenation was simulated using Aspen Plus.⁶⁴ Hydrogen was produced by the electrolysis of water using carbon-free source of energy. Energy for carbon capture and methanol plants was provided from the coal-based power plant itself. The detailed design of the components of the methanol plant such as reactor, distillation column and heat exchangers were included in the simulation model. Furthermore, pinch analysis-based heat exchanger network design was implemented in Aspen Energy Analyzer. Aspen exchanger design and rating (Aspen EDR) was used for the design of all individual heat exchangers. Methanol plant provided significant share of energy (46% of steam necessary) to CO₂ capture by chemical absorption, which substantially reduced the capture impact on the power plant economics. Large reduction in CO₂ emissions was possible if carbon-free hydrogen source was chosen. The process was modified⁶⁵ by optimizing the compression network.

The integration of captured CO₂ (PCCC from flue gas of power plant) with natural gas reforming plant for methanol production was presented.¹⁶³ This integration reduced the methane consumption by 25.6% and CO₂ emissions by 21.9%. The product to feed ratio was also improved from 1.69 (for conventional) to 2.27. The methanol synthesis route by CO₂ utilization integrated with EGR and geo-sequestration was investigated considering several process configurations.¹⁶⁴ The performance of methanol synthesis was evaluated in terms of intensity of CH₄ and CO₂, thermal energy intensity, methanol productivity, and CO₂ uptake flexibility. The proposed methanol production configuration was found

to consume natural gas with up to 23.2% (mole) CO₂. Furthermore, the highest CO₂ abatement intensity (45.5%) was found by EGR and using geo-sequestration.

A complex electrochemical reduction model of CO₂ to formic acid or formate¹⁶⁵ was simulated using gPROMS. The system was analyzed based on the cell height and electrode properties. Five times better performance was observed by using electrode catalyst (hypothetical electrode of the electrochemical cell) as compared to the experimental results. In another study, the model of an elevated pressure CO₂ electrolyzer for formic acid production was reported using MATLAB.¹⁶⁶ The current density was strongly affected by pressure while faradaic and energy efficiencies were found to be independent of pressure above 20 bar. A DME synthesis by tri reforming of biogas was simulated in Aspen Plus¹⁶⁷ and it was shown that this process must be operated above 800°C, carbon to steam ratio of 2, and oxygen to carbon ratio of 0.1. Efficiency of the process was significantly improved on removal of both water and CO₂.

More sustainable routes to abate atmospheric CO₂ should be explored and identified to improve the overall economics and to reduce the carbon footprints. A summary of the discussion presented in this section is summarized in Table 6. Although process modeling and simulation is a powerful tool to assess processes from thermodynamic and economic point of view, these studies are based on certain assumptions. Assumptions should be realistic and technically correct. Moreover, in CO₂ utilization process modeling, economic estimations are not found in most of the articles. Future research should probe economic evaluation of these processes so that an idea about their sustainability could be made.

3.5 | Process optimization

Optimization plays a vital role at various levels in process and power industry. Some of the examples of optimization include improving the yield of product, reducing the yield of contaminants, reducing the energy consumption, improving the efficiency of process, minimizing the resources required for a given task and selection of the most suitable pathway and supply chain. Optimization of CO₂ utilization processes is a major field of interest nowadays to mitigate carbon with the minimum economic impact. Superstructure-based optimization is used by several researchers and are discussed in this section. Various routes for CO₂ utilization are available, some of them are already implemented at commercial scale (e.g., urea production) while some are under development stages (e.g., microalgae cultivation). Optimization problems formulated by researchers regarding CO₂ utilization

are mainly divided into following two categories, (1) optimization of existing processing route (e.g., selection of optimal operating conditions), (2) selecting the most economical processing route out of all the available options. A representative superstructure for a general CCU process optimization is shown in Figure 9.

3.5.1 | Optimization of existing process routes

Already developed CO₂ utilization processes are under consideration to increase the net profit or to decrease the net emissions. Most of the CO₂ utilization processes (e.g., methanol production by CO₂ hydrogenation) are not economically feasible right now (as already discussed). Optimization of existing processes can reduce their economic burden. Direct production of DME from syngas was optimized with the objective to maximize the DME production rate in a fixed bed reactor using differential evolution (DE) algorithm.¹⁷⁰ Number of tubes in the reactor, temperature of feed and coolant water temperature were optimized. The optimization resulted in reactor design that yielded 4.84% more DME as compared to conventional reactors used for DME production along with 4.62% decrease in number of tubes of the reactor. A pipe shell reactor was optimized for DME production from syngas.¹⁷¹ The optimized reactor design resulted in lower value of hot spot temperature which provided better functionality of bi-functional catalyst. Dry and mixed reforming of methane processes were optimized by modeling the reactor in UniSim Design Suite.¹⁷² At optimum conditions, the requirement of a compact reactor and consequently lower capital and operating costs were found.

Dynamic optimization was performed to optimize the recycle ratio of CO₂ and shell coolant temperature under certain process constraints for a Lurgi type methanol reactor.¹⁷³ For this purpose, a hybrid algorithm was used by combining genetic algorithm (GA) and generalized pattern search (GPS). CO₂ recycle ratios of 0% and 5% increased the methanol production by 1.67% and 2.53%, respectively using optimal temperature. A biofilm growth model was used to maximize the utilization of CO₂ and biomass production.¹⁷⁴ The optimizing variables were gas flow rate, number of biofilm reactors installed in series, and gas composition. The model was also validated with the experimental data. The maximum CO₂ utilization efficiency of 96% was found with 25 or more biofilm reactors connected in series. The concentrated CO₂ stream with plug flow behavior was identified to be a critical factor for high CO₂ utilization and biomass production.

Mixed integer nonlinear programming (MINLP)-based synthesis model was formulated¹⁷⁵ to maximize the CO₂

TABLE 6 Modeling and simulation of CO₂ utilization processes

Sr. #	Utilization/Sequestration pathway	Performance parameter	Parameter studied	Software used	Reference
1	Syngas	CO ₂ conversion and energy requirement	Operating conditions and flowrate of CO ₂	Aspen Plus®	[147]
2	CO ₂ as gasifying agent	Exergy efficiency & energy conversion efficiency	Feed composition (raw wood, torrefied wood & coal) and steam to carbon ratio	Aspen Plus V8.4®	[148]
3	Methanol	Methanol yield	H ₂ /CO ₂ molar ratio, pressure, temperature and adsorbent volume capacity	Aspen Plus®	[149]
4	Methanol	CO ₂ conversion, methanol production, yield & selectivity	CO addition to feed, recycle, operating temperature & membrane presence	Aspen Plus® and MS Excel	[150]
5	Syngas	Conversion of CH ₄ and CO ₂	Catalyst, reactant ratio & reaction temp.	Aspen Plus®	[151]
6	Biofuel	Biomass to fuel conversion process	Economic feasibility and environmental impacts	Aspen Process Economic Analyzer®	[152]
7	EGS	Process economics	Drilling cost, plant lifetime and thermal drawdown rate	EURONAUT and GEOPHORES	[153]
8	EOR	Process economics	CO ₂ injection, oil production and cost	CO ₂ -PROPHET	[154]
9	Calcium carbonate	Power & heat demand of various routes, and cost estimate	Various routes for conversion of calcium silicate to carbonate	Aspen Plus®	[168]
10	Urea & electricity	CO ₂ utilized & process economics	Conversion of WGSR & auxiliary power	Aspen Plus®	[169]
11	DMC	Performance evaluation of four routes of CO ₂ conversion to DMC	Yield of DMC, energy consumption, CO ₂ emissions, global warming potential	Aspen Plus®	[155]
12	Syngas & CH ₄	PtS and PtM scenarios evaluation	Economic evaluation parameters and CO ₂ concentration in feed	Aspen Plus™	[156]
13	Methane and ammonia	Product prices (electricity, methane and ammonia)	Capture level, production variation (due to demand variations) and price variation	Aspen Plus®	[157]
14	Methanol	Methanol yield and production cost (fixed & operating)	Operating temperature and pressure, methanol selling price, oxygen sale	Aspen Plus®	[158]
15	Methanol	Cost per unit production of methanol	Operating temperature and pressure, flowsheet modifications & carbon balance	Aspen Plus®	[17]
15	Methanol	CO ₂ conversion, process economy & net GHG emissions	Energy integration, hydrogen production, methanol price & price of electricity	Aspen Plus®	[18]
16	DME	Climate change potential (CCP) and technical assessment	Operating conditions, process configuration (conventional, CCU and CCS)	Aspen Plus®	[159]

TABLE 6 (Continued)

Sr. #	Utilization/Sequestration pathway	Performance parameter	Parameter studied	Software used	Reference
17	Methanol	CO ₂ conversion and methanol selectivity	Reactor type	FORTRAN95	[160]
18	DME	Power output and DME yield	Operating conditions & syngas conversion	PRO/II® v8.1.1	[161]
19	Methanol	CO ₂ capture and conversion	Heat integration, CO ₂ emissions	Aspen Plus®	[64]
20	Methanol	CO ₂ capture and conversion	Heat integration, CO ₂ emissions & process modifications	Aspen Plus®	[65]
21	Urea and methanol	CO ₂ emissions	Product purity, CO ₂ conversion, CO ₂ emissions, product yield, thermal and electrical energy requirement	Chemcad™	[26]
22	Methanol	Reactor design, methanol production and CO ₂ utilization	Reaction rates, operating conditions and recycle	UniSim Design Suite	[162]
23	Methanol	Product to feed ratio	NG and CO ₂ consumption	Aspen Plus V 8.4®	[163]
24	Methanol & EGR	CO ₂ abatement intensity	Energy consumption, CH ₃ OH production	Aspen Plus®	[164]
25	Formic acid	Formate production and current density	Geometry constraints, liquid flowrate, pressure and inlet concentrations	gPROMS ModelBuilder v4.0	[165]
26	Formic acid	Performance of CO ₂ electrolyzer	Pressure, Faradaic efficiency, current density and energy supplied to electrolyzer	MATLAB	[166]
27	DME	Process efficiency	Reformer temperature, Steam/Carbon ratio, O/C ratio, recycle and removal of water and CO ₂	Aspen Plus®	[167]

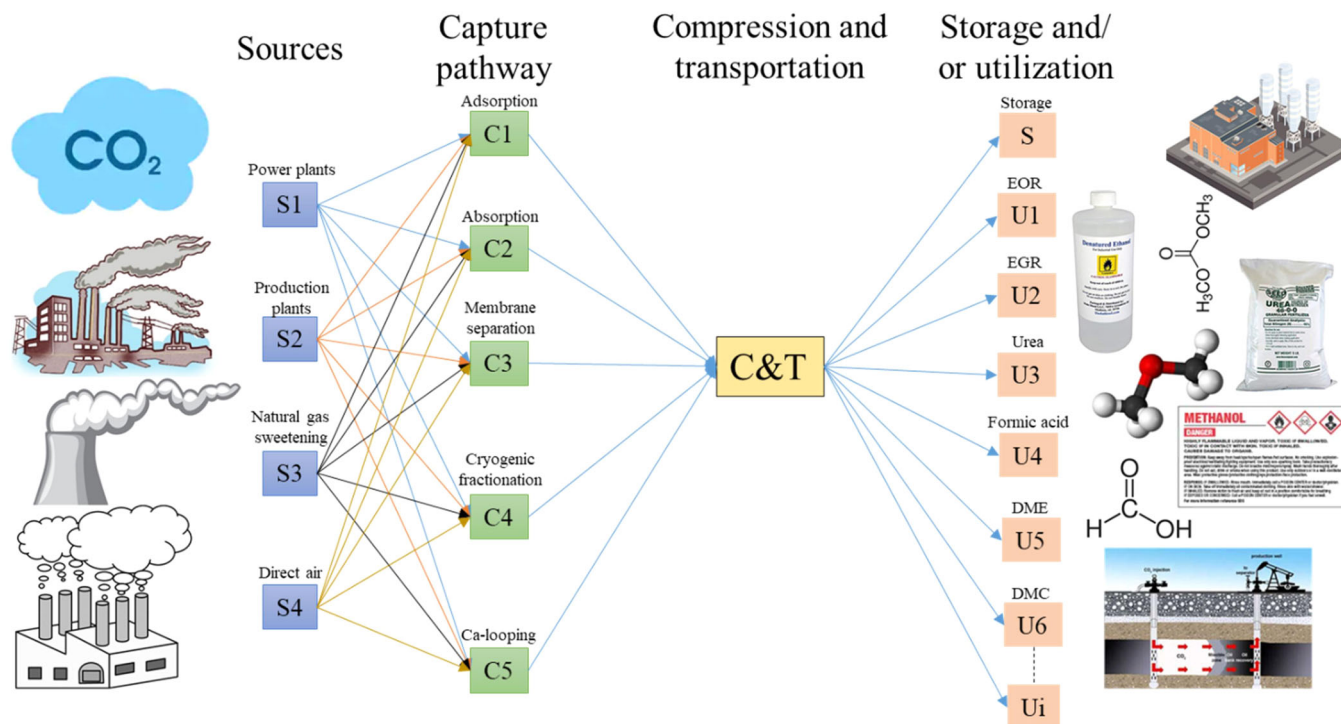


FIGURE 9 A general superstructure of CCU

utilization and syngas selectivity. Reforming technologies for the thermochemical conversion of CO_2 to syngas using both rigorous and reduced reactors were considered, and the optimization problem was implemented in GAMS using ANTIGONE solver. Partial oxidation and dry reforming (PODR) were found to possess more potential for converting CO_2 to syngas with 100% conversion of CO_2 when syngas ratio (H_2/CO) lies in the range of 1–1.7. While for the syngas ratios up to 2.4, the combination of dry reforming (DR), combined dry and steam methane reforming (CDSMR), and tri reforming (TR) was found to be the most effective. For further higher syngas ratios, a combination of steam methane reforming (SMR), tri reforming (TR) and RWGS exhibited the highest potential of CO_2 conversion. MIP model to optimize carbon capture and storage/utilization versus carbon trading for fossil fuel-based power plants in Turkey was formulated.¹⁷⁶ EOR was considered as utilization option and data for two CFPPs from different parts of Turkey was used. The model was solved in GAMS and the obtained results showed that CCU should be prioritized in Turkey to mitigate carbon in an environmentally friendly and economic way.

3.5.2 | Selection of processing routes

Apart from optimization of existing CO_2 utilization processes, optimization can also be used to find the

optimal processing route from all the possible routes. The purpose of such optimization studies mainly includes the reduction in GHG emissions along with increased net profit. A multiperiod stochastic model for optimizing CCS infrastructure was formulated,¹⁷⁷ which was aimed at meeting CO_2 mitigation target while maximizing the profit. The stochastic parameters used rendered the model more realistic. The model was solved using GAMS for 20 years' interval from 2011 to 2030 to identify most profitable way for carbon capture, utilization and storage (CCUS) in Korea. Various processing routes are possible for microalgae production at large scale and the optimal route was selected out of 7800 routes by minimizing the cost and GHG emissions using superstructure-based approach.¹⁷⁸ In another study, a supply chain superstructure based MILP model was developed, incorporating comprehensive transportation routes and system deployment schemes.¹⁷⁹ Objective of the model was to optimize CCUS for EOR process in Northeast China over a period of 20 years. The optimization resulted in 50% reduction of current CO_2 emissions at total annual cost of \$2.30 billion and \$0.77 billion annual revenues from EOR.

A framework to analyze sustainability of various CCU routes using superstructure-based approach (similar to one presented in Figure 9) was developed.²⁰ An indigenous computational tool ArKa-TAC³ was demonstrated for both techno-economic and CO_2 reduction analyses in a convenient and faster way. The tool was

demonstrated by analyzing the acetic acid production and evaluating the sustainability of CCU process in four different countries. Another superstructure-based MINLP optimization model was formulated to maximize the net profit and minimize the GHG emissions.¹⁸⁰ Optimal solution was affected by scale of CO₂ emission source, market demand of the product and product pricing. The optimal solution was also observed to vary from region to region and the mathematical model developed can also be applied in designing an optimal CCU supply chain network.

The literature discussed above is summarized in Table 7. The table represents the objectives of each study along with model type, parameters studied, utilization option, and solver/algorithm used. Optimization of CO₂ utilization process can give huge benefits in terms of increased net profit and reduced GHG emissions. Optimization is a very strong tool in finding the most cost-effective way of mitigating global warming and such studies should be extended to other CO₂ utilization processes as well. Such studies could also be used to predict the future decisions and to forecast future actions. Previous optimization studies have taken some assumptions (e.g., neglecting the emissions from utilities and transportation of products) which makes the problem less complicated but introduces uncertainty in the results. The uncertainty introduced in the results depends upon the assumptions taken to simplify the optimization problem. Unrealistic assumptions in the optimization study may result in deviation of the results from the system boundaries, violation of science and engineering rules, deviation from the data profiles of the system, and so forth. Robust optimization and stochastic programming are the techniques used to handle uncertain optimization studies.¹⁸¹ It is also proposed to neglect unrealistic assumptions in future works, this will no doubt increase the computational power and complicate the problem yielding more and more realistic results.

4 | CONCLUSIONS AND FUTURE RECOMMENDATIONS

The mitigation of CO₂ is a challenge for researchers due to its environmental and economic impacts. CCS has been an attractive option from last two decades. However, CCS technologies are not feasible because of their economic drawbacks. The focus of researchers is shifting toward CO₂ utilization to get economic benefits along with CO₂ mitigation. In this way, the captured CO₂ can be utilized to produce valuable end products. Being a highly stable molecule, CO₂ requires elevated conditions of temperature and pressure for its conversion which

needs substantial amounts of energy. This energy demand for CO₂ utilization can be reduced by using special catalysts. The current status and challenges for CO₂ utilization are presented in this article from thermodynamic, economic and environmental point of view. The advancements and improvements in CO₂ utilization have been critically analyzed using the quantitative and qualitative information obtained from experimental and computational studies. The selection of a specific CO₂ utilization process is a multidimensional problem as it depends on several factors and requires the information of potential product market, environmental, economic, and technological feasibility. All the related information has been presented in the form of pictorial representations and tabulated data. The multiscale perspective has been discussed in a broad spectrum starting from molecular simulations to superstructure-based approaches. Nevertheless, the major focus was perspective of PSE. The following conclusions may be drawn from this critical review of the current status and challenges for CO₂ utilization.

- Integration of CO₂ utilization with the capture plant may improve the overall economics. However, the economic feasibility of both processes needs improvement in terms of energy penalty and capital investments.
- All the physical utilization processes of CO₂ (except EGS) are considered mature technologies and can sequester large volumes of CO₂ for long period of time. However, carbonated beverages, fire extinguishers and dry ice do not actually sequester CO₂ as ultimate fate of the gas utilized by these processes is its emission back to environment.
- Methane has the highest potential to mitigate CO₂. However, currently most of the global methane is extracted from natural gas wells. As natural gas reserves are depleting continuously, the future of CO₂ utilization for methane production is bright. The CO₂ utilization potential of ethanol, methanol and syngas is also significantly higher but economic feasibility of these processes is a question.
- Hydrogen is the key ingredient that is required in most of the chemical utilization processes including methanol synthesis, ethanol synthesis, syngas production, DME production, DMC production, and so forth. Economics of hydrogen production have significant impact on sustainability of these processes.
- If economics of methane, ethanol, methanol, and syngas production are improved, these processes have the potential to be used as feedstock for other processes and in this way their future demand may significantly increase. This will in turn increase the utilization of CO₂.

TABLE 7 Role of process optimization in CCU processes

Sr. #	Utilization/ Sequestration option	Objectives	Parameters studied	Model type	Software used	Implementation	Reference
1	DME production	Maximize rate of DME production	Number of reactor tubes, feed inlet conditions and coolant temperature	DE	MATLAB	n/a	[170]
2	DME production	Identification of optimal process conditions	DME selectivity, CO conversion, hot spot temperature	Balances and constitutive relations	(RK method)	n/a	[171]
3	Syngas production	Trade-off between maximum CO ₂ consumption and methanol production	Operating conditions	ODEs	UniSim Design Suite	n/a	[172]
4	Methanol synthesis	Maximize methanol production	Shell coolant temperature & CO ₂ recycle ratio	Hybrid GA-GPS	---	n/a	[173]
5	Microalgae cultivation	Maximize CO ₂ utilization & biomass production	Gas flow rate, gas composition & number of reactors	ODEs	MATLAB	n/a	[174]
6	Syngas production	Maximize CO ₂ utilization & syngas selectivity	Reactor type for reforming reaction	MINLP	MATLAB and GAMS	n/a	[175]
7	EOR	Carbon mitigation for power plants in Turkey	Reduced CO ₂ emissions	MIP	GAMS	Soma and Afsin, Turkey	[176]
8	Various CCU options	Economic benefit & life cycle GHG reduction	CO ₂ emission, product pricing, and operating cost	Stochastic	GAMS	n/a	[177]
9	Microalgae cultivation	Minimize overall cost and GHG emissions	Biofuel production and biological carbon sequestration	MINLP	GAMS	n/a	[178]
10	EOR	Minimize CO ₂ emissions & maximizing profit	CO ₂ capture, transportation, utilization & economic parameters	MILP	GAMS	Northeast China	[179]
11	Acetic acid	Maximizing net profit & minimizing CO ₂ emissions	Economic parameters, processing route	MIP	ArKa-TAC ³	n/a	[20]
12	Various CCU options	Minimize emissions while maximizing profit	CO ₂ emission, market demand and product pricing	LP	MS Excel	n/a	[180]

- Only a few chemical utilization processes are mature and well-developed including production of salicylic acid, methanol, urea, polycarbonates, and polyurethane. Some of the processes are in the mid of their development stages, for example, algae, calcium carbonate, formic acid, methane, syngas, sodium carbonate, DMC and propylene carbonate while others are in starting stages of their development including acetic acid, ethanol, magnesium carbonate, carbamates and DME.
- Appropriate catalyst development is a major challenge for the less developed processes, for example, low product yield is an issue for ethanol production.
- Various levels of PSE techniques are playing important role in exploring new pathways, design improvements and energy efficiency improvements. Nevertheless, the contribution of molecular level simulations, CFD and policy level analysis is limited in this field.
- LCA studies presented MgCO₃ production, DMC production, methanol production, EOR and biodiesel production from microalgae as the environmentally sustainable options among CO₂ utilization processes while formic acid production through CO₂ utilization route is not economically feasible.
- Integration of different processes can reduce the net energy requirements and can improve the economics of integrated processes. For example, integration of CO₂ capture with utilization processes can reduce power requirement of stripper of capture plant (e.g., in case of methanol production process).
- Process optimization is a powerful tool that can reduce the costs associated with existing processes and can also be used to select the optimized processing path out of the potential pathways.
- CO₂ utilization is a vast field which is under exploration in wide areas from multiple fronts for improving the economic and environmental impacts.

CO₂ utilization provides an attractive opportunity for reducing global warming potential of several industrial sectors. CO₂ utilization projects should be implemented on large scale for economic benefits concurrently reducing CO₂ emissions. Based on the literature presented in this article, following are the suggestions for future actions.

- Assess all chemical utilization processes for their technical, economic and environmental feasibility. This should lead to link further processes which in turn will be facilitated by the chemicals obtained from CO₂ utilization processes to assess and forecast the overall potential of CO₂ utilization and its economic and environmental feasibility.
- More focus should be given to the development of novel catalysts for conversion of CO₂ to reduce the

high energy requirements, for example, considering the example of methane production which have significant CO₂ reduction potential, but the catalytic performance of this process should be improved for its implementation at industrial scale.

- Molecular simulations should be used to explore and analyze the chemical CO₂ utilization by identifying the reaction mechanisms and molecular affinity in the presence of catalyst.
- The use of CFD simulations to improve the operating conditions, the design of reactors and to gain the information about mechanisms occurring within the process, for example, the complex integration of hydrodynamics, photo dynamics, cell growth and mass transfer is the major barrier behind the design of commercial reactors for microalgae cultivation. As the CFD models are generally more accurate and can involve various complex phenomena along with reactor designs, therefore, these models could be used to gain the insights for design and operation improvement with great accuracy.
- Energy integration and optimization of the existing power plants with CCU plants for mitigating climate changes should be investigated for economic feasibility. Moreover, EGS systems using CO₂ as working fluid should be optimized to improve its economics.
- Hydrogen is used as a raw material in many chemical CO₂ utilization processes including methanol, ethanol, DME, DMC and methane production. Its economics must be improved to improve the overall economics of CO₂ utilization especially by utilizing renewable energy.

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REFERENCES

1. Polvani G, Marsh LM, Stenke DR, et al. The response of the ozone layer to quadrupled CO₂. *J Clim*. 2018;31(10): 3893-3907. doi:10.1175/JCLI-D-17-0492.1

2. Jiang J, Ye B, Liu J. Research on the peak of CO₂ emissions in the developing world: current progress and future prospect. *Appl Energ.* 2019;235:186-203. doi:10.1016/j.apenergy.2018.10.089
3. Le C, Moriarty R, Andrew RM, et al. Global carbon budget 2014. *Earth Syst Sci Data.* 2015;7(1):47-85. doi:10.5194/essd-7-47-2015
4. Friedlingstein P, O'Sullivan M, Jones MW, et al. Global carbon budget 2020. *Earth Syst Sci Data.* 2020;12(4):3269-3340. doi:10.5194/ESSD-12-3269-2020
5. Jessica B, Arndt DS. State of the climate in 2018. *Bull Am Meteor Soc.* 2019;100(9):Si-S306. doi:10.1175/2019BAMSStateoftheClimate.1
6. Shieber J. CO₂ in the atmosphere just exceeded 415 parts per million for the first time in human history. *TechCrunch.* 2019. Accessed November 24, 2019. <https://techcrunch.com/2019/05/12/co2-in-the-atmosphere-just-exceeded-415-parts-per-million-for-the-first-time-in-human-history>
7. IEA. Emissions by sector—greenhouse gas emissions from energy: Overview—Analysis. IEA. 2021. Accessed October 20, 2021. <https://www.iea.org/reports/greenhouse-gas-emissions-from-energy-overview/emissions-by-sector#abstract>
8. Raghuvanshi SP, Chandra A, Raghav AK. Carbon dioxide emissions from coal based power generation in India. *Energy Convers Manag.* 2006;47(4):427-441. doi:10.1016/j.enconman.2005.05.007
9. Arif A, Rizwan M, Elkamel A, Hakeem L, Zaman M. Optimal selection of integrated electricity generation systems for the power sector with low greenhouse gas (GHG) emissions. *Energies.* 2020;13(17):4571. doi:10.3390/EN13174571
10. Notton G, Nivet ML, Voyant C, et al. Intermittent and stochastic character of renewable energy sources: consequences, cost of intermittence and benefit of forecasting. *Renew Sustain Energy Rev.* 2018;87:96-105. doi:10.1016/J.RSER.2018.02.007
11. Zaman M, Lee JH. Carbon capture from stationary power generation sources: a review of the current status of the technologies. *Korean J Chem Eng.* 2013;30(8):1497-1526.
12. Streit JE, Hillis RR. Estimating fault stability and sustainable fluid pressures for underground storage of CO₂ in porous rock. *Energy.* 2004;29(9-10):1445-1456. doi:10.1016/j.energy.2004.03.078
13. Zhang L, Huang H, Wang Y, et al. CO₂ storage safety and leakage monitoring in the CCS demonstration project of Jilin oilfield, China. *Greenh Gases Sci Technol.* 2014;4(4):425-439. doi:10.1002/ghg.1411
14. Irlam L. Global costs of carbon capture and storage 2017 update. *Global CCS Institute.* 2017.
15. Mac Dowell N, Fennell PS, Shah N, Maitland GC. The role of CO₂ capture and utilization in mitigating climate change. *Nat Clim Chang.* 2017;7(4):243-249. doi:10.1038/nclimate3231
16. Bruhn T, Naims H, Olfe-Kräutlein B. Separating the debate on CO₂ utilisation from carbon capture and storage. *Environ Sci Pol.* 2016;60:38-43. doi:10.1016/j.envsci.2016.03.001
17. Yousaf M, Mahmood A, Elkamel A, Rizwan M, Zaman M. Techno-economic analysis of integrated hydrogen and methanol production process by CO₂ hydrogenation. *Int J Greenh Gas Control.* 2022;115:103615. doi:10.1016/J.IJGGC.2022.103615
18. Meunier N, Chauvy R, Mouhoubi S, Thomas D, De Weireld G. Alternative production of methanol from industrial CO₂. *Renew Energy.* 2020;146:1192-1203. doi:10.1016/j.renene.2019.07.010
19. Hakeem L, Khan MA, Rizwan M, Elkamel A. A multi-period optimization model for power sector with CO₂ emission considerations. *Int. J. Energy Res.* 2021;46(3):14505-14516. doi:10.3390/en13174571
20. Roh K, Lim H, Chung W, Oh J, Yoo H, Al-Hunaidy AS, Imran H, Lee JH. Sustainability analysis of CO₂ capture and utilization processes using a computer-aided tool. *J CO₂ Util.* 2018;26:60-69. doi:10.1016/j.jcou.2018.04.022
21. Pearson RJ, Eisaman MD, Turner JWG, Edwards PP, Jiang Z, Kuznetsov VL, Littau KA, Di ML, Taylor SRG. Energy storage via carbon-neutral fuels made from CO₂, water, and renewable energy. *Proc IEEE.* 2012;100(2):440-460. doi:10.1109/JPROC.2011.2168369
22. Hagen DL. Methanol: its synthesis, use as a fuel, economics, and hazards. National Technical Information Service. 1976. <https://ntrl.ntis.gov/NTRL/dashboard/searchResults/titleDetail/NP21727.xhtml>
23. Olah GA. Beyond oil and gas: the methanol economy. *Angew Chemie—Int Ed.* 2005;44(18):2636-2639. doi:10.1002/anie.200462121
24. Chapman AM, Keyworth C, Kember MR, Lennox AJJ, Williams CK. Adding value to power station captured CO₂: tolerant Zn and Mg homogeneous catalysts for polycarbonate polyol production. *ACS Catal.* 2015;5(3):1581-1588. doi:10.1021/cs501798s
25. Morinaga T, Kawada N. The production of acetic acid from carbon dioxide and hydrogen by an anaerobic bacterium. *J Biotechnol.* 1990;14(2):187-194. doi:10.1016/0168-1656(90)90007-X
26. Pérez-Fortes M, Bocin-Dumitriu A, Tzimas E. CO₂ utilization pathways: techno-economic assessment and market opportunities. *Energy Procedia.* 2014;63(i):7968-7975. doi:10.1016/j.egypro.2014.11.834
27. Andrei M, De Simoni M, Delbianco A, Cazzani P, Zanibelli L. Enhanced oil recovery with CO₂ capture and sequestration. 2010. Accessed November 27, 2019. <https://www.researchgate.net/publication/265025822>
28. Porqueras EM, Rittmann S, Herwig C. Biofuels and CO₂ neutrality: an opportunity. *Biofuels.* 2012;3(4):413-426. doi:10.4155/bfs.12.25
29. Sven B, Eshel A. Photosynthesis of *Ulva* sp. II. Utilization of CO₂ and HCO₃⁻ when submerged. *J Exp Mar Bio Ecol.* 1983;70(1):99-106. doi:10.1016/0022-0981(83)90152-1
30. Nahar S, Zain MFM, Kadhum AAH, Hasan HA, Hasan MR. Advances in photocatalytic CO₂ reduction with water: a review. *Materials.* 2017;10(6):629. doi:10.3390/ma10060629
31. Castro S, Albo J, Irabien A. Photoelectrochemical reactors for CO₂ utilization. *ACS Sustain Chem Eng.* 2018;6(12):15877-15894. doi:10.1021/acssuschemeng.8b03706
32. Alper E, Orhan OY. CO₂ utilization: developments in conversion processes. *Petroleum.* 2017;3(1):109-126. doi:10.1016/j.petlm.2016.11.003
33. Saeidi S, Amin NAS, Rahimpour MR. Hydrogenation of CO₂ to value-added products—a review and potential future

- developments. *J CO₂ Util.* 2014;5:66-81. doi:10.1016/j.jcou.2013.12.005
34. Zimmermann AW, Schomäcker R. Assessing early-stage CO₂ utilization technologies—comparing apples and oranges? *Energy Technol.* 2017;5(6):850-860. doi:10.1002/ente.201600805
35. Al-Mamoori A, Krishnamurthy A, Rownaghi AA, Rezaei F. Carbon capture and utilization update. *Energy Technol.* 2017;5(6):834-849. doi:10.1002/ente.201600747
36. Tapia JFD, Lee J-Y, Ooi REH, Foo DCY, Tan RR. A review of optimization and decision-making models for the planning of CO₂ capture, utilization and storage (CCUS) systems. *Sustain Prod Consum.* 2018;13:1-15. doi:10.1016/j.spc.2017.10.001
37. Aresta M, Dibenedetto A, Angelini A. The changing paradigm in CO₂ utilization. *J CO₂ Util.* 2013;3-4:65-73. doi:10.1016/j.jcou.2013.08.001
38. Huang CH, Tan CS. A review: CO₂ utilization. *Aerosol Air Qual Res.* 2014;14(2):480-499. doi:10.4209/aaqr.2013.10.0326
39. Hu J, Galvita VV, Poelman H, Marin GB. Advanced chemical looping materials for CO₂ utilization: a review. *Materials.* 2018;11(7):1187. doi:10.3390/ma11071187
40. Norhasyima RS, Mahlia TMI. Advances in CO₂ utilization technology: a patent landscape review. *J CO₂ Util.* 2018;26:323-335. doi:10.1016/j.jcou.2018.05.022
41. Pan S-Y, Ling T-C, Park A-HA, Chiang P-C. An overview: reaction mechanisms and modelling of CO₂ utilization via mineralization. *Aerosol Air Qual Res.* 2018;18(4):829-848. doi:10.4209/aaqr.2018.03.0093
42. Rafiee A, Rajab Khalilpour K, Milani D, Panahi M. Trends in CO₂ conversion and utilization: a review from process systems perspective. *J Environ Chem Eng.* 2018;6(5):5771-5794. doi:10.1016/j.jece.2018.08.065
43. Cuéllar-Franca RM, Azapagic A. Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts. *J CO₂ Util.* 2015;9:82-102. doi:10.1016/j.jcou.2014.12.001
44. Zhao S, Feron P, Deng L, et al. Status and progress of membrane contactors in post-combustion carbon capture: a state-of-the-art review of new developments. *J Membr Sci.* 2016;511:180-206. doi:10.1016/j.memsci.2016.03.051
45. Leeson D, Mac Dowell N, Shah N, Petit C, Fennell PS. A techno-economic analysis and systematic review of carbon capture and storage (CCS) applied to the iron and steel, cement, oil refining and pulp and paper industries, as well as other high purity sources. *Int J Greenh Gas Control.* 2017;61:71-84. doi:10.1016/j.ijggc.2017.03.020
46. Habib MA, Badr HM, Ahmed SF, et al. A review of recent developments in carbon capture utilizing oxy-fuel combustion in conventional and ion transport membrane systems. *Int J Energy Res.* 2011;35(9):741-764. doi:10.1002/er.1798
47. (Henry) Liang Z, Rongwong W, Liu H, et al. Recent progress and new developments in post-combustion carbon-capture technology with amine based solvents. *Int J Greenh Gas Control.* 2015;40:26-54. doi:10.1016/j.ijggc.2015.06.017
48. Kunze C, Spliethoff H. Assessment of oxy-fuel, pre- and post-combustion-based carbon capture for future IGCC plants. *Appl Energy.* 2012;94:109-116. doi:10.1016/j.apenergy.2012.01.013
49. Andrei M, Simoni MD, Delbianco A, Cazzani P, Zanibelli L. Enhanced Oil Recovery with CO₂ Capture and Sequestration. *World Energy Congr.* 2010:1-20. <https://www.researchgate.net/publication/265025822>
50. Acetic Acid Market Benefits from Surge in Asian Chemical Industry and Technological Innovations, GBI Research. (accessed Sep. 13, 2022). <https://www.gbiresearch.com/media-center/press-releases/acetic-acid-market-benefits-from-surge-in-asian-chemical-industry-and-technological-innovations>
51. Global Acrylic Acid Market Set For Rapid Growth, Market Research Store. (accessed Sep. 13, 2022). <https://www.marketresearchstore.com/news/global-acrylic-acid-market-143>
52. Chauvy R, Meunier N, Thomas D, De Weireld G. Selecting emerging CO₂ utilization products for short- to mid-term deployment. *Appl Energy.* 2019;236:662-680. doi:10.1016/j.apenergy.2018.11.096
53. Aresta M, Dibenedetto A, Quaranta E. State of the art and perspectives in catalytic processes for CO₂ conversion into chemicals and fuels: the distinctive contribution of chemical catalysis and biotechnology. *J Catal.* 2016;343:2-45. doi:10.1016/j.jcat.2016.04.003
54. Otto A, Grube T, Schiebahn S, Stolten D. Closing the loop: captured CO₂ as a feedstock in the chemical industry. *Energy Environ Sci.* 2015;8(11):3283-3297. doi:10.1039/c5ee02591e
55. Juillet. Valorisation chimique du CO₂. *L'Agence l'Environnement la Maîtrise l'Energie.* 2014.
56. Hands R. Market Drivers for the Syngas Industry. *Gasification and Syngas Technology Council. Gasification.* 2017.
57. Aresta M, Dibenedetto A, Angelini A. Catalysis for the valorization of exhaust carbon: from CO₂ to chemicals, materials, and fuels, technological use of CO₂ *Chem Rev.* 2014;114(3):1709-1742. doi:10.1021/cr4002758
58. Brown T. Urea production is not carbon sequestration—ammonia industry. 2016. Accessed September 5, 2020. <https://ammoniaindustry.com/urea-production-is-not-carbon-sequestration/>
59. Brinckerhoff P. *Accelerating uptake CCS industrial use captured carbon dioxide.* Global CCS Institute. 2011. <https://www.globalccsinstitute.com/archive/hub/publications/14026/accelerating-uptake-ccs-industrial-use-captured-carbon-dioxide.pdf>
60. Koohestanian E, Sadeghi J, Mohebbi-Kalhari D, Shahraki F, Samimi A. A novel process for CO₂ capture from the flue gases to produce urea and ammonia. *Energy.* 2018;144:279-285. doi:10.1016/j.energy.2017.12.034
61. Zhu W, Michalsky R, Metin Ö, et al. Monodisperse Au nanoparticles for selective electrocatalytic reduction of CO₂ to CO. *J Am Chem Soc.* 2013;135(45):16833-16836. doi:10.1021/ja409445p
62. Ni M. An electrochemical model for syngas production by co-electrolysis of H₂O and CO₂. *J Power Sources.* 2012;202:209-216. doi:10.1016/j.jpowsour.2011.11.080
63. Verhelst S, Turner JW, Sileghem L, Vancoillie J. Methanol as a fuel for internal combustion engines. *Progr Energy Combust Sci.* 2019;70:43-88. doi:10.1016/j.peccs.2018.10.001
64. Van-Dal ÉS, Bouallou C. CO₂ abatement through a methanol production process. *Chem Eng Trans.* 2012;29(2006):463-468. doi:10.3303/CET1229078

65. Van-Dal ÉS, Bouallou C. Design and simulation of a methanol production plant from CO₂ hydrogenation. *J Clean Prod.* 2013;57:38-45. doi:10.1016/j.jclepro.2013.06.008
66. Miaohua C. Agricultural ecology and varied functional synthetical uses of methane. *J Guangxi Teach Educ Univ (Natural Sci. Ed.)*. 2015;36(6):154-161. doi:10.1016/j.jelechem.2012.11.033
67. Olsson L, Hahn-Hägerdal B. Fermentation of lignocellulosic hydrolysates for ethanol production. *Enzyme Microb Technol.* 1996;18(5):312-331. doi:10.1016/0141-0229(95)00157-3
68. Dias De Oliveira ME, Vaughan BE, Rykiel EJ. Ethanol as fuel: energy, carbon dioxide balances, and ecological footprint. *BioScience.* 2005;55(7):593-602. doi:10.1641/0006-3568(2005)055[0593:EAFCED]2.0.CO;2
69. Arcoumanis C, Bae C, Crookes R, Kinoshita E. The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: a review. *Fuel.* 2008;87(7):1014-1030. doi:10.1016/j.fuel.2007.06.007
70. Rumayor M, Dominguez-ramos A. Formic acid manufacture: carbon dioxide utilization alternatives. *Appl Sci.* 2018;8(6):914. doi:10.3390/app8060914
71. Wei T, Wang M, Wei W, Sun Y, Zhong B. Synthesis of dimethyl carbonate by transesterification over CaO/carbon solid base catalysts. *Stud Surf Sci Catal.* 2004;153:41-46. doi:10.1016/s0167-2991(04)80217-9
72. Department of Energy. Algae-to-Fuel; 2020
73. Algae Basics - Benefits of Algae. Accessed September 13, 2022. <http://allaboutalgae.com/benefits/>
74. Liang Y. Producing liquid transportation fuels from heterotrophic microalgae. *Appl Energ.* 2013;104:860-868. doi:10.1016/j.apenergy.2012.10.067
75. Leach AR. *Molecular Modelling: Principles and Applications*. Prentice Hall; 2001.
76. Perez-Blanco ME, Maginn EJ. Molecular dynamics simulations of carbon dioxide and water at an ionic liquid interface. *J Phys Chem B.* 2011;115(35):10488-10499. doi:10.1021/jp203838j
77. Cygan RT, Romanov VN, Myshakin EM. Molecular simulation of carbon dioxide capture by montmorillonite using an accurate and flexible force field. *J Phys Chem C.* 2012;116(24):13079-13091. doi:10.1021/jp3007574
78. Wang T, Xie H, Song Z, et al. Role of hydrogen bond capacity of solvents in reactions of amines with CO₂: a computational study. *J Environ Sci.* 2020;91:271-278. doi:10.1016/j.jes.2020.01.019
79. Babarao R, Dai S, Jiang D-E. Nitrogen-doped mesoporous carbon for carbon capture—a molecular simulation study. *J Phys Chem C.* 2012;116(12):7106-7110. doi:10.1021/jp301450m
80. Liu Y, Wilcox J. Molecular simulation studies of CO₂ adsorption by carbon model compounds for carbon capture and sequestration applications. *Environ Sci Technol.* 2013;47(1):95-101. doi:10.1021/es3012029
81. Liu B, Wang C, Zhang J, et al. Displacement mechanism of oil in shale inorganic nanopores by supercritical carbon dioxide from molecular dynamics simulations. *Energy Fuels.* 2017;31(1):738-746. doi:10.1021/acs.energyfuels.6b02377
82. Fang T, Wang M, Gao Y, Zhang Y, Yan Y, Zhang J. Enhanced oil recovery with CO₂/N₂ slug in low permeability reservoir: molecular dynamics simulation. *Chem Eng Sci.* 2019;197:204-211. doi:10.1016/j.ces.2018.12.016
83. Takbiri-Borujeni A, Kazemi M, Liu S, Zhong Z. Molecular simulation of enhanced oil recovery in shale. *Energy Procedia.* 2019;158:6067-6072. doi:10.1016/j.egypro.2019.01.510
84. Pathak M, Huang H, Meakin P, Deo M. Molecular investigation of the interactions of carbon dioxide and methane with kerogen: application in enhanced shale gas recovery. *J Nat Gas Sci Eng.* 2018;51:1-8. doi:10.1016/j.jngse.2017.12.021
85. Liu J, Xi S, Chapman WG. Competitive sorption of CO₂ with gas mixtures in nanoporous shale for enhanced gas recovery from density functional theory. *Langmuir.* 2019;35(24):8144-8158. doi:10.1021/acs.langmuir.9b00410
86. Hu X, Deng H, Lu C, Tian Y, Jin Z. Characterization of CO₂/CH₄ competitive adsorption in various clay minerals in relation to shale gas recovery from molecular simulation. *Energy Fuels.* 2019;33(9):8202-8214. doi:10.1021/acs.energyfuels.9b01610
87. Kattel S, Yan B, Yang Y, Chen JG, Liu P. Optimizing binding energies of key intermediates for CO₂ hydrogenation to methanol over oxide-supported copper. *J Am Chem Soc.* 2016;138(38):12440-12450. doi:10.1021/JACS.6B05791/ASSET/IMAGES/LARGE/JA-2016-05791Z_0010.JPEG
88. Samson K, Sliwa M, Socha RP, et al. Influence of ZrO₂ structure and copper electronic state on activity of Cu/ZrO₂ catalysts in methanol synthesis from CO₂. *ACS Catal.* 2014;4(10):3730-3741. doi:10.1021/CS500979C/SUPPL_FILE/CS500979C_SI_002.PDF
89. Maulana AL, Putra RID, Saputro AG, et al. DFT and microkinetic investigation of methanol synthesis via CO₂ hydrogenation on Ni(111)-based surfaces. *Phys Chem Chem Phys.* 2019;21(36):20276-20286. doi:10.1039/C9CP02970B
90. Peng G, Sibener SJ, Schatz GC, Mavrikakis M. CO₂ hydrogenation to formic acid on Ni(110). *Surf Sci.* 2012;606(13-14):1050-1055. doi:10.1016/j.susc.2012.02.027
91. Wang H, Nie X, Chen Y, Guo X, Song C. Facet effect on CO₂ adsorption, dissociation and hydrogenation over Fe catalysts: insight from DFT. *J CO₂ Util.* 2018;26:160-170. doi:10.1016/J.JCOU.2018.05.003
92. Choi S, Sang BI, Hong J, et al. Catalytic behavior of metal catalysts in high-temperature RWGS reaction: in-situ FT-IR experiments and first-principles calculations. *Sci Rep.* 2017;7(1):1-10. doi:10.1038/srep41207
93. Torrie GM, Valleau JP. Nonphysical sampling distributions in Monte Carlo free-energy estimation: umbrella sampling. *J Comput Phys.* 1977;23(2):187-199. doi:10.1016/0021-9991(77)90121-8
94. Blazek J. *Computational Fluid Dynamics: Principles and Applications*. 3rd ed. Elsevier Ltd; 2015.
95. Deng ZG, Xiao R, Jin BS, Song QL, Huang H. Multiphase CFD modeling for a chemical looping combustion process (fuel reactor). *Chem Eng Technol.* 2008;31(12):1754-1766. doi:10.1002/ceat.200800341
96. Asendrych D, Niegodajew P, Drobniak S. CFD modelling of CO₂ capture in a packed bed by chemical absorption. *Chem Process Eng—Inz Chem i Process.* 2013;34(2):269-282. doi:10.2478/cpe-2013-0022

97. Breault RW, Huckaby ED. Parametric behavior of a CO₂ capture process: CFD simulation of solid-sorbent CO₂ absorption in a riser reactor. *Appl Energy*. 2013;112:224-234. doi:10.1016/j.apenergy.2013.06.008
98. Ghadirian E, Abbasian J, Arastoopour H. Three-dimensional CFD simulation of an MgO-based sorbent regeneration reactor in a carbon capture process. *Powder Technol*. 2017;318:314-320. doi:10.1016/j.powtec.2017.06.012
99. Ryan EM, DeCroix D, Breault R, Xu W, Huckaby ED, Saha K, Dartevelle S, Sun X. Multi-phase CFD modeling of solid sorbent carbon capture system. *Powder Technol*. 2013;242:117-134. doi:10.1016/j.powtec.2013.01.009
100. Edge PJ, Heggs PJ, Pourkashanian M, Stephenson PL. Integrated fluid dynamics-process modelling of a coal-fired power plant with carbon capture. *Appl Therm Eng*. 2013;60(1-2):242-250. doi:10.1016/j.applthermaleng.2013.06.024
101. Liu F, Ellett K, Xiao Y, Rupp JA. Assessing the feasibility of CO₂ storage in the New Albany Shale (Devonian-Mississippian) with potential enhanced gas recovery using reservoir simulation. *Int J Greenh Gas Control*. 2013;17:111-126. doi:10.1016/j.ijggc.2013.04.018
102. Khan C, Amin R, Madden G. Carbon dioxide injection for enhanced gas recovery and storage (reservoir simulation). *Egypt J Pet*. 2013;22(2):225-240. doi:10.1016/j.ejpe.2013.06.002
103. White MD, McPherson BJ, Grigg RB, Ampomah W, Appold MS. Numerical simulation of carbon dioxide injection in the western section of the farnsworth unit. *Energy Procedia*. 2014;63:7891-7912. doi:10.1016/j.egypro.2014.11.825
104. Safi R, Agarwal RK, Banerjee S. Numerical simulation and optimization of CO₂ utilization for enhanced oil recovery from depleted reservoirs. *Chem Eng Sci*. 2016;144:30-38. doi:10.1016/j.ces.2016.01.021
105. Pruess K. On the production behavior of enhanced geothermal systems with CO₂ as working fluid. *Energy Convers. Manag*. 2008;49(6):1446-1454. doi:10.1016/J.ENCONMAN.2007.12.029
106. Zhang W, Machida H, Takano H, Izumiya K, Norinaga K. Computational fluid dynamics simulation of CO₂ methanation in a shell-and-tube reactor with multi-region conjugate heat transfer. *Chem Eng Sci*. 2020;211:115276. doi:10.1016/j.ces.2019.115276
107. Lee B, Yun SW, Kim S, Heo J, Kim YT, Lee S, Lim H. CO₂ reforming of methane for H₂ production in a membrane reactor as CO₂ utilization: computational fluid dynamics studies with a reactor geometry. *Int J Hydrogen Energy*. 2019;44(4):2298-2311. doi:10.1016/J.IJHYDENE.2018.09.184
108. Bian Z, Xia H, Wang Z, et al. CFD simulation of a hydrogen-permeable membrane reactor for CO₂ reforming of CH₄: the interplay of the reaction and hydrogen permeation. *Energy Fuels*. 2020;34(10):12366-12378. doi:10.1021/ACS.ENERGYFUELS.0C02333/ASSET/IMAGES/MEDIUM/EF0C02333_M023.GIF
109. Pavličič A, Huš M, Prašnikar A, Likozar B. Multiscale modelling of CO₂ reduction to methanol over industrial Cu/ZnO/Al₂O₃ heterogeneous catalyst: linking ab initio surface reaction kinetics with reactor fluid dynamics. *J Clean Prod*. 2020;275:122958. doi:10.1016/J.JCLEPRO.2020.122958
110. Brusseau ML. Sustainable development and other solutions to pollution and global change. In: Brusseau ML, Pepper IL, Gerba CP, eds. *Environmental and Pollution Science*. Elsevier; 2019:585-603.
111. Finnveden G, Hauschild MZ, Ekvall T, et al. Recent developments in life cycle assessment. *J Environ Manage*. 2009;91(1):1-21. doi:10.1016/j.jenvman.2009.06.018
112. ISO. *ISO 14040 International Standard*; 2006
113. Müller LJ, Kätelhön A, Bachmann M, Zimmermann A, Sternberg A, Bardow A. A guideline for life cycle assessment of carbon capture and utilization. *Front Energy Res*. 2020;8:15. doi:10.3389/fenrg.2020.00015
114. Khoo HH, Sharratt PN, Bu J, et al. Carbon capture and mineralization in Singapore: preliminary environmental impacts and costs via LCA. *Ind Eng Chem Res*. 2011;50(19):11350-11357. doi:10.1021/ie200592h
115. Nduagu E, Bergerson J, Zevenhoven R. Life cycle assessment of CO₂ sequestration in magnesium silicate rock—a comparative study. *Energy Convers Manag*. 2012;55:116-126. doi:10.1016/j.enconman.2011.10.026
116. Aresta M, Galatola M. Life cycle analysis applied to the assessment of the environmental impact of alternative synthetic processes. The dimethylcarbonate case: part 1. *J Clean Prod*. 1999;7(3):181-193. doi:10.1016/S0959-6526(98)00074-2
117. Von Der Assen N, Jung J, Bardow A. Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls. *Energy Environ Sci*. 2013;6(9):2721-2734. doi:10.1039/c3ee41151f
118. Sternberg A, Jens CM, Bardow A. Life cycle assessment of CO₂-based C1-chemicals. *Green Chem*. 2017;19(9):2244-2259. doi:10.1039/c6gc02852g
119. Aldaco R, Butnar I, Margallo M, et al. Bringing value to the chemical industry from capture, storage and use of CO₂: a dynamic LCA of formic acid production. *Sci Total Environ*. 2019;663:738-753. doi:10.1016/j.scitotenv.2019.01.395
120. Ahn Y, Byun J, Kim D, Kim BS, Lee CS, Han J. System-level analysis and life cycle assessment of CO₂ and fossil-based formic acid strategies. *Green Chem*. 2019;21(12):3442-3455. doi:10.1039/c9gc01280j
121. Hertwich EG, Aaberg M, Singh B, Strømman AH. Life-cycle assessment of carbon dioxide capture for enhanced oil recovery. *Chinese J Chem Eng*. 2008;16(3):343-353. doi:10.1016/S1004-9541(08)60085-3
122. Jaramillo P, Griffin WM, McCoy ST. Life cycle inventory of CO₂ in an enhanced oil recovery system. *Environ Sci Technol*. 2009;43(21):8027-8032. doi:10.1021/es902006h
123. Lardon L, Hélias A, Sialve B, Steyer JP, Bernard O. Life-cycle assessment of biodiesel production from microalgae. *Environ Sci Technol*. 2009;43(17):6475-6481. doi:10.1021/es900705j
124. Campbell PK, Beer T, Batten D. Life cycle assessment of biodiesel production from microalgae in ponds. *Bioresour Technol*. 2011;102(1):50-56. doi:10.1016/j.biortech.2010.06.048
125. Brentner LB, Eckelman MJ, Zimmerman JB. Combinatorial life cycle assessment to inform process design of industrial

- production of algal biodiesel. *Environ Sci Technol*. 2011;45(16):7060-7067. doi:10.1021/es2006995
126. Clarens AF, Nassau H, Resurreccion EP, White MA, Colosi LM. Environmental impacts of algae-derived biodiesel and bioelectricity for transportation. *Environ Sci Technol*. 2011;45(17):7554-7560. doi:10.1021/es200760n
 127. Soratana K, Khanna V, Landis AE. Re-envisioning the renewable fuel standard to minimize unintended consequences: a comparison of microalgal diesel with other biodiesels. *Appl Energy*. 2013;112:194-204. doi:10.1016/j.apenergy.2013.05.082
 128. Zimmermann AW, Müller L, Wang Y, et al. Techno-economic assessment & life cycle assessment guidelines for CO₂ utilization (Version 1.1). *Glob. CO₂ initiat*. 2020. doi:10.3998/2027.42/162573
 129. Björklund AE. Survey of approaches to improve reliability in LCA. *Int J Life Cycle Assess*. 2002;7(2):64-72. doi:10.1007/BF02978849
 130. Morgan JC, Soares CA, Omell B, et al. Development of a rigorous modeling framework for solvent-based CO₂ capture. part 2: steady-state validation and uncertainty quantification with pilot plant data. *Ind Eng Chem Res*. 2018;57(31):10464-10481. doi:10.1021/acs.iecr.8b01472
 131. Gabrielsen J, Svendsen HF, Michelsen ML, Stenby EH, Kontogeorgis GM. Experimental validation of a rate-based model for CO₂ capture using an AMP solution. *Chem Eng Sci*. 2007;62(9):2397-2413. doi:10.1016/j.ces.2007.01.034
 132. Zaman M, Lee JH, Gani R. Carbon dioxide capture processes: simulation, design and sensitivity analysis. *12th International Conference on Control, Automation and Systems*, IEEE. 2012:539-544. <https://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&number=6393241&isnumber=6393028>
 133. Alhajaj A, Mac Dowell N, Shah N. A techno-economic analysis of post-combustion CO₂ capture and compression applied to a combined cycle gas turbine: part I. A parametric study of the key technical performance indicators. *Int J Greenh Gas Control*. 2016;44:26-41. doi:10.1016/j.ijggc.2015.10.022
 134. Ali U, Agbonghae EO, Hughes KJ, Ingham DB, Ma L, Pourkashanian M. Techno-economic process design of a commercial-scale amine-based CO₂ capture system for natural gas combined cycle power plant with exhaust gas recirculation. *Appl Therm Eng*. 2016;103:747-758. doi:10.1016/j.applthermaleng.2016.04.145
 135. Vaccarelli M, Carapellucci R, Giordano L. Energy and economic analysis of the CO₂ capture from flue gas of combined cycle power plants. *Energy Procedia*. 2014;45:1165-1174. doi:10.1016/j.egypro.2014.01.122
 136. Zhang X, Song Z, Gani R, Zhou T. Comparative economic analysis of physical, chemical, and hybrid absorption processes for carbon capture. *Ind Eng Chem Res*. 2020;59(5):2005-2012. doi:10.1021/acs.iecr.9b05510
 137. Dubois L, Thomas D. Simulations of various configurations of the post-combustion CO₂ capture process applied to a cement plant flue gas: parametric study with different solvents. *Energy Procedia*. 2017;114:1409-1423. doi:10.1016/j.egypro.2017.03.1265
 138. Obek CA, Ayittey FK, Saptorio A. 2019. Improved process modifications of aqueous ammonia-based CO₂ capture system. In: *MATEC Web of Conferences*, EDP Sciences; Vol 268; 2004. doi:10.1051/MATECONF/201926802004
 139. Ramzan N, Shakeel U, Gungor A, Zaman M. Techno-economic analysis of selexol and sulfinol processes for pre-combustion CO₂ capture. *2018 International Conference on Power Generation Systems and Renewable Energy Technologies (PGSRET)*, IEEE; 2018:1-6. doi:10.1109/PGSRET.2018.8686026
 140. Taheri M, Dai C, Lei Z. CO₂ capture by methanol, ionic liquid, and their binary mixtures: experiments, modeling, and process simulation. *AIChE J*. 2018;64(6):2168-2180.
 141. Plaza MG, Rubiera F. Evaluation of a novel multibed heat-integrated vacuum and temperature swing adsorption post-combustion CO₂ capture process. *Appl Energy*. 2019;250:916-925. doi:10.1016/j.apenergy.2019.05.079
 142. Zaman M, Lee JH. Optimization of the various modes of flexible operation for post-combustion CO₂ capture plant. *Comput Chem Eng*. 2015;75:14-27. doi:10.1016/j.compchemeng.2014.12.017
 143. Zaman M, Jang H, Rizwan M, Lee JH. Optimal design for flexible operation of the post-combustion CO₂ capture plant with uncertain economic factors. *Comput Chem Eng*. 2016;84:199-207. doi:10.1016/j.compchemeng.2015.09.002
 144. Bui M, Flø NE, de Cazenove T, Mac Dowell N. Demonstrating flexible operation of the technology centre mongstad (TCM) CO₂ capture plant. *Int J Greenh Gas Control*. 2020;93:102879. doi:10.1016/j.ijggc.2019.102879
 145. Chan LLT, Chen J. Improving the energy cost of an absorber-stripper CO₂ capture process through economic model predictive control. *Int J Greenh Gas Control*. 2018;76:158-166. doi:10.1016/j.ijggc.2018.05.018
 146. Wu X, Wang M, Shen J, Li Y, Lawal A, Lee KY. Reinforced coordinated control of coal-fired power plant retrofitted with solvent based CO₂ capture using model predictive controls. *Appl Energy*. 2019;238:495-515. doi:10.1016/j.apenergy.2019.01.082
 147. Renganathan T, Yadav MV, Pushpavanam S, Voolapalli RK, Cho YS. CO₂ utilization for gasification of carbonaceous feedstocks: a thermodynamic analysis. *Chem Eng Sci*. 2012;83:159-170. doi:10.1016/j.ces.2012.04.024
 148. Kuo PC, Wu W. Thermodynamic analysis of a combined heat and power system with CO₂ utilization based on co-gasification of biomass and coal. *Chem Eng Sci*. 2016;142:201-214. doi:10.1016/j.ces.2015.11.030
 149. Zachopoulos A, Heracleous E. Overcoming the equilibrium barriers of CO₂ hydrogenation to methanol via water sorption: a thermodynamic analysis. *J CO₂ Util*. 2017;21:360-367. doi:10.1016/j.jcou.2017.06.007
 150. Leonzio G. Methanol synthesis: optimal solution for a better efficiency of the process. *Processes*. 2018;6(3):20. doi:10.3390/pr6030020
 151. Roy PS, Song J, Kim K, Park CS, Raju ASK. CO₂ conversion to syngas through the steam-biogas reforming process. *J CO₂ Util*. 2018;25:275-282. doi:10.1016/j.jcou.2018.04.013
 152. Sharifzadeh M, Wang L, Shah N. Integrated biorefineries: CO₂ utilization for maximum biomass conversion. *Renew Sustain Energy Rev*. 2015;47:151-161. doi:10.1016/j.rser.2015.03.001

153. Olasolo P, Juárez MC, Olasolo J, Morales MP, Valdani D. Economic analysis of Enhanced Geothermal Systems (EGS). A review of software packages for estimating and simulating costs. *Appl Thermal Eng.* 2016;104:647-658. doi:10.1016/j.applthermaleng.2016.05.073
154. Fukai I, Mishra S, Moody MA. Economic analysis of CO₂-enhanced oil recovery in Ohio: implications for carbon capture, utilization, and storage in the Appalachian Basin region. *Int J Greenh Gas Control.* 2016;52:357-377. doi:10.1016/j.ijggc.2016.07.015
155. Kongpanna P, Pavarajarn V, Gani R, Assabumrungrat S. Techno-economic evaluation of different CO₂-based processes for dimethyl carbonate production. *Chem Eng Res Des.* 2015;93:496-510. doi:10.1016/j.cherd.2014.07.013
156. Chiuta S, Engelbrecht N, Human G, Bessarabov DG. Techno-economic assessment of power-to-methane and power-to-syngas business models for sustainable carbon dioxide utilization in coal-to-liquid facilities. *J CO₂ Util.* 2016;16:399-411. doi:10.1016/j.jcou.2016.10.001
157. Sheikh HM, Ullah A, Hong K, Zaman M. Thermo-economic analysis of integrated gasification combined cycle (IGCC) power plant with carbon capture. *Chem Eng Process—Process Intensif.* 2018;128:53-62. doi:10.1016/j.cep.2018.04.007
158. Bellotti D, Dierks M, Moellenbruck F, Magistri L, Görner K, Oeljeklaus G. Thermodynamic and economic analysis of a plant for the CO₂ hydrogenation for methanol production. *E3S Web Conf.* 2019;113:01013. doi:10.1051/E3SCONF/201911301013
159. Schakel W, Oreggioni G, Singh B, Strømman A, Ramírez A. Assessing the techno-environmental performance of CO₂ utilization via dry reforming of methane for the production of dimethyl ether. *J CO₂ Util.* 2016;16:138-149. doi:10.1016/j.jcou.2016.06.005
160. Gallucci F, Basile A. A theoretical analysis of methanol synthesis from CO₂ and H₂ in a ceramic membrane reactor. *Int J Hydrogen Energy.* 2007;32(18):5050-5058. doi:10.1016/j.ijhydene.2007.07.067
161. Chen P-C, Yu C-S, Chiu H-M, Chyou Y-P, Chen H-J. Process simulation study of coal gasification-based multi-product plant with electricity and chemical products. *Asia-Pacific J Chem Eng.* 2012;7:S101-S111. doi:10.1002/apj.657
162. Park N, Park MJ, Ha KS, Lee YJ, Jun KW. Modeling and analysis of a methanol synthesis process using a mixed reforming reactor: perspective on methanol production and CO₂ utilization. *Fuel.* 2014;129:163-172. doi:10.1016/j.fuel.2014.03.068
163. Milani D, Khalilpour R, Zahedi G, Abbas A. A model-based analysis of CO₂ utilization in methanol synthesis plant. *J CO₂ Util.* 2015;10:12-22. doi:10.1016/j.jcou.2015.02.003
164. Luu MT, Milani D, Abbas A. Analysis of CO₂ utilization for methanol synthesis integrated with enhanced gas recovery. *J Clean Prod.* 2016;112:3540-3554. doi:10.1016/j.jclepro.2015.10.119
165. Georgopoulou C, Jain S, Agarwal A, et al. On the modelling of multidisciplinary electrochemical systems with application on the electrochemical conversion of CO₂ to formate/formic acid. *Comput Chem Eng.* 2016;93:160-170. doi:10.1016/j.compchemeng.2016.06.012
166. Morrison ART, van Beusekom V, Ramdin M, van den Broeke LJP, Vlugt TJH, de Jong W. Modeling the electrochemical conversion of carbon dioxide to formic acid or formate at elevated pressures. *J Electrochem Soc.* 2019;166:E77. doi:10.1149/2.0121904jes
167. Saebea D, Authayanun S, Arpornwichanop A. Process simulation of bio-dimethyl ether synthesis from tri-reforming of biogas: CO₂ utilization. *Energy.* 2019;175:36-45. doi:10.1016/j.energy.2019.03.062
168. Teir S, Eloneva S, Zevenhoven R. Production of precipitated calcium carbonate from calcium silicates and carbon dioxide. *Energy Convers Manag.* 2005;46(18-19):2954-2979. doi:10.1016/j.enconman.2005.02.009
169. Bose A, Jana K, Mitra D, De S. Co-production of power and urea from coal with CO₂ capture: performance assessment. *Clean Technol Environ Pol.* 2015;17(5):1271-1280. doi:10.1007/s10098-015-0960-7
170. Vakili R, Eslamloueyan R. Design and optimization of a fixed bed reactor for direct dimethyl ether production from syngas using differential evolution algorithm. *Int J Chem React Eng.* 2013;11(1):147-158. doi:10.1515/ijcre-2012-0026
171. Hu Y, Nie Z, Fang D. Simulation and model design of pipe-shell reactor for the direct synthesis of dimethyl ether from syngas. *J Nat Gas Chem.* 2008;17(2):195-200. doi:10.1016/S1003-9953(08)60051-1
172. Park N, Park MJ, Baek SC, et al. Modeling and optimization of the mixed reforming of methane: maximizing CO₂ utilization for non-equilibrated reaction. *Fuel.* 2014;115:357-365. doi:10.1016/j.fuel.2013.07.035
173. Alarifi A, Liu Z, Erenay FS, Elkamel A, Croiset E. Dynamic optimization of lurgi type methanol reactor using hybrid GA-GPS algorithm: the optimal shell temperature trajectory and carbon dioxide utilization. *Ind Eng Chem Res.* 2016;55(5):1164-1173. doi:10.1021/acs.iecr.5b02918
174. Blanken W, Schaap S, Theobald S, Rinzema A, Wijffels RH, Janssen M. Optimizing carbon dioxide utilization for microalgae biofilm cultivation. *Biotechnol Bioeng.* 2017;114(4):769-776. doi:10.1002/bit.26199
175. Balasubramanian P, Bajaj I, Hasan MMF. Simulation and optimization of reforming reactors for carbon dioxide utilization using both rigorous and reduced models. *J CO₂ Util.* 2018;23:80-104. doi:10.1016/j.jcou.2017.10.014
176. Ağralı S, Üçtuğ FG, Türkmen BA. An optimization model for carbon capture & storage/utilization vs. carbon trading: a case study of fossil-fired power plants in Turkey. *J Environ Manage.* 2018;215:305-315. doi:10.1016/j.jenvman.2018.03.054
177. Han J-H, Lee I-B. Multiperiod stochastic optimization model for carbon capture and storage infrastructure under uncertainty in CO₂ emissions, product prices, and operating costs. *Ind Eng Chem Res.* 2012;51(35):11445-11457. doi:10.1021/ie3004754
178. Gong J, You F. Global optimization for sustainable design and synthesis of algae processing network for CO₂ mitigation and biofuel production using life cycle

- optimization. *AIChE J.* 2014;60(9):3195-3210. doi:10.1002/aic.14504
179. Zhang S, Liu L, Zhang L, Zhuang Y, Du J. An optimization model for carbon capture utilization and storage supply chain: a case study in northeastern China. *Appl Energy.* 2018;231:194-206. doi:10.1016/j.apenergy.2018.09.129
180. Roh K, Al-Hunaidy AS, Imran H, Lee JH. Optimization-based identification of CO₂ capture and utilization processing paths for life cycle greenhouse gas reduction and economic benefits. *AIChE J.* 2019;65(7). doi:10.1002/aic.16580
181. Klamroth K, Köbis E, Schöbel A, Tammer C. A unified approach to uncertain optimization. *Eur J Oper Res.* 2017;260(2):403-420. doi:10.1016/j.ejor.2016.12.045

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