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REVIEW

# Carbon dioxide utilization: A critical review from multiscale perspective

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## Abstract

Carbon dioxide ($CO_2$) emissions contribute considerably towards increasing greenhouse effect. Carbon capture and storage can reduce $CO_2$ emissions to a great extent but lacks economic feasibility. The economic feasibility of $CO_2$ capture could be boosted by utilizing the captured gas to produce valuable end products. $CO_2$ 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 $CO_2$ 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, $CO_2$ utilization, greenhouse gas emissions, process systems engineering, sustainability

## 1 | INTRODUCTION

The high concentration of carbon dioxide ($CO_2$) in the stratosphere hinders the formation of new ozone molecules and therefore, contributes toward greenhouse effect.[1] Moreover, the concentration of $CO_2$ 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 $CO_2$ emissions. But afterward, rapid growth of industrialization in the world caused a significant increase in $CO_2$ emissions, especially from anthropogenic sources.[3] The atmospheric growth of $CO_2$ 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 2019[4] as shown in Figure 1. National Oceanic and Atmospheric Administration (NOAA) and American Meteorological Society (AMS) reported the global atmospheric $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ emissions.

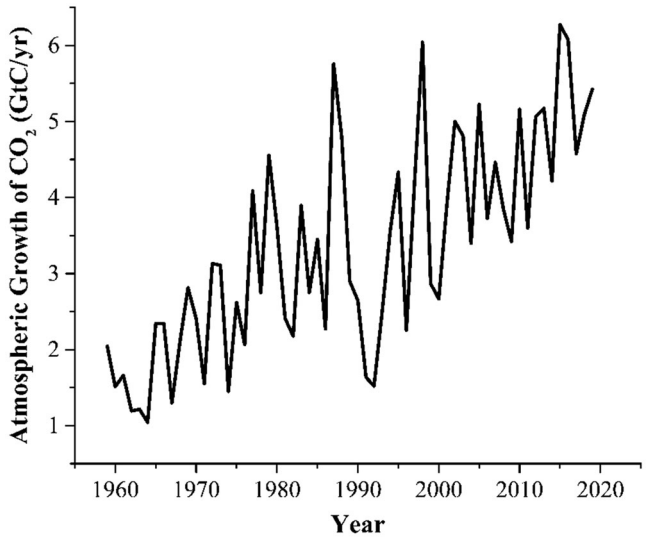


FIGURE 1 Atmospheric growth of $CO_2$. *Source*: Reproduced from Friedlingstein et al.[4]

The GHGs (prominently $CO_2$) 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 $CO_2$-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, $CO_2$ 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 $CO_2$ may create surface stability issues or false permeation leading to leakages and thus, emitting the captured $CO_2$ 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] $CO_2$ utilization is now considered as the most feasible option available and focus is shifting toward the production of valuable products from $CO_2$.[15] It could significantly help to reduce the cost of $CO_2$ storage as well as recover the cost of carbon capture, and can improve the overall economy of the process.[16] Integration of $CO_2$ capture process with some of the $CO_2$ utilization processes (e.g., hydrogenation of $CO_2$ to methanol) and doing energy integrations, the energy required for capture process can be reduced thus reducing the cost of $CO_2$ capture.[17,18] Currently, the $CO_2$ utilization processes require energy input in the form of heat, pressure and/or catalyst for the activation of highly stable $CO_2$ molecule, this is the reason behind the economic infeasibility of most of $CO_2$ utilization processes. Nevertheless, $CO_2$ 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) $CO_2$ availability, (2) product demand, (3) product price, (4) process economics, and (5) overall environmental impact. The main objectives of the $CO_2$ utilization process are net $CO_2$ and cost reduction.[20] Various studies on $CO_2$ utilization routes have been reported in the literature. Utilization of captured $CO_2$ is mainly in the (1) production of carbon-neutral fuels that do not emit net $CO_2$ 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 $CO_2$ 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) $CO_2$ can also be utilized through photosynthesis by growing more plants[29] 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 $CO_2$ reduction,[30,31] $CO_2$ utilization through carboxylation and reduction reactions,[32] hydrocarbon and methanol synthesis,[33] assessing early-stage $CO_2$ utilization technologies,[34] current status, challenges and roadmap for the further development of $CO_2$ utilization technologies,[35–37] cultivation of microalgae using $CO_2$ and hydrogenation of $CO_2$ to energy products,[38] advanced chemical looping materials (i.e., metal oxide-based materials) for $CO_2$ utilization,[39] review of patents on $CO_2$ utilization technologies published between 1980 and 2017,[40] overview of reaction mechanisms and catalyst activities for $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization.

In this article, a comprehensive review of $CO_2$ 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 $CO_2$ utilization process (for further research or industrial implementation) is a critical decision, many process parameters like lifecycle inventory, $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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

$CO_2$ 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 $CO_2$ sequestration because of their potential to store large volumes of $CO_2$.[49] $CO_2$ 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 $CO_2$ (by changing the molecular identity) as most of the physical utilization processes stores $CO_2$ 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 $CO_2$. 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, $CO_2$ mitigation potentials, and related issues or challenges.

### 2.1 | Physical utilization

During physical utilization, $CO_2$ remains in pure form either suspended in a solution or have its own distinguished existence. These processes exploit the physical properties of $CO_2$ for its utilization, for example, solubility of $CO_2$ endorsed its use in carbonated beverages. Numerous industrial applications are known in which $CO_2$ can be physically consumed; prominent ones are sketched in Figure 2. This section presents the processes for physical utilization of $CO_2$ 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 $CO_2$ molecule's identity in chemical utilization does not exist in the end products as it is transformed into some other compound. $CO_2$ is extensively used in chemical industry especially as

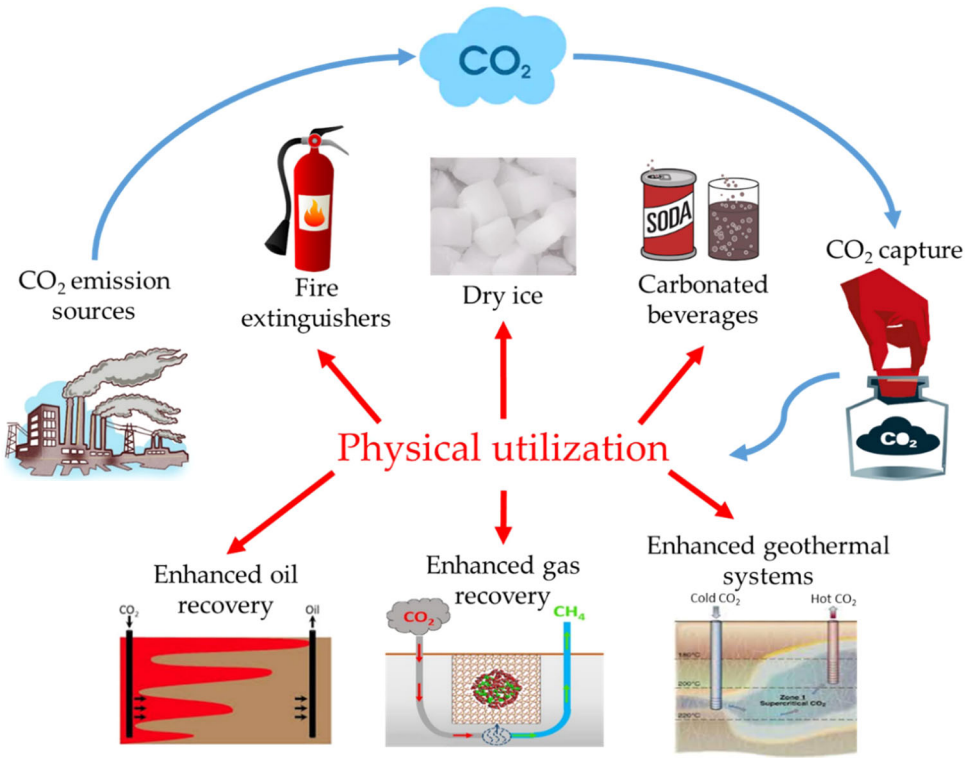


FIGURE 2 Physical $CO_2$ utilization processes

TABLE 1 Summary of various physical $CO_2$ utilization processes

| Utilization/ sequestration option | Pros | Cons | TRL |
|---|---|---|---|
| Enhanced oil recovery | • Large volume of $CO_2$ can be sequestered permanently<br>• Increases oil production from oil fields<br>• Economically favorable process especially when carbon tax is implemented | • Due to low viscosity of $CO_2$ oil recovery is less compared to other working fluids<br>• The trapped $CO_2$ in the wells can leak back to the atmosphere which is a serious concern | 9 |
| Enhanced gas recovery | • Large volume of $CO_2$ can be sequestered permanently<br>• Increased gas production from gas wells<br>• Due to density and viscosity differences, mixing of $CO_2$ and $CH_4$ can be avoided (at high methane concentrations) | • Separation of natural gas from injected $CO_2$ (when natural gas concentration is low) is an issue and requires additional processing<br>• The trapped $CO_2$ in the wells can leak back to the atmosphere which poses a serious concern | 9 |
| Enhanced geothermal systems | Compared to water:<br>• Increased heat recovery from hot rocks<br>• $CO_2$ leakage in rocks is favorable as it do not create stability issues | • Very deep drilling is required for EGS<br>• Economically infeasible for commercial applications | 5 |
| Carbonated beverages | • Adds value to beverages taste<br>• Consumption of $CO_2$ in beverages can improve capture process economy | • No sequestration of $CO_2$<br>• Too much consumption of carbonated beverages has serious health impacts | 9 |
| Dry ice | • Dry ice has got advantage of lower temperature than ice<br>• It does not leave any residue behind (like water in case of ice) | • Too much lower temperature is dangerous<br>• Ultimate addition of $CO_2$ to the atmosphere when it sublimes | 9 |
| Fire extinguishers | • Good fire extinguishing characteristics<br>• Best suited for electrical fires<br>• No harmful residues left behind | • Ultimate addition of $CO_2$ to the atmosphere<br>• They cannot be used for solid fuel burning fires | 9 |

a feedstock for the production of various chemicals and synthetic fuels. $CO_2$ 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 $CO_2$ are carried over metallic catalysts and still high temperature and pressure conditions are required for its conversion. However, economics of the reaction pathways using $CO_2$ 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 $CO_2$ utilization as huge volumes of $CO_2$ 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 $CO_2$. Moreover, in doing economic analysis or energy conservation, the net reduction in overall $CO_2$ footprint should be realized along with economic benefits.

Several options are available to convert $CO_2$ 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 $CO_2$. Selection of $CO_2$ utilization process for its implementation is a critical decision. Most important parameters that must be analyzed before selection of $CO_2$ utilization process includes market demand of the end product, $CO_2$ reduction potential, raw material availability, and economic feasibility.

Annual production of various chemicals and fuels along with their stoichiometric $CO_2$ uptake potentials and TRLs (if produced by $CO_2$ conversion) are presented in Table 2. Stoichiometric $CO_2$ 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 $CO_2$. It should be realized that these stoichiometric $CO_2$ uptake potentials does not incorporate the emissions associated with processing intervals; however, these data may provide an overview of reduction in $CO_2$ 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] |

$CO_2$ 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 $CO_2$ achieved if all the current production of target product is from $CO_2$. 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 $CO_2$ uptake is calculated if all the production amount of methane is manufactured from industrial process utilizing $CO_2$. Industrial production of methane is not a mature technology and TRL mentioned here is for the industrial process that can utilize $CO_2$. Furthermore, the production terms presented in Table 2 contain current overall production which may be increased if the economy of $CO_2$ 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.

$CO_2$ 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 $CO_2$.[58] This carbon footprint can be slightly reduced by using $CO_2$ from reformer flue gas as reactant in the process.[59] Integration of urea production plant with power plant or other $CO_2$ emission sources can reduce the carbon footprint by using $CO_2$ emitted as feedstock for urea production. A novel process for coproduction of urea and electricity from power plants was proposed in which $CO_2$ 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 $CO_2$ consumed. Utilization of $CO_2$ for urea production is a mature technology and it has the potential to mitigate significant $CO_2$ if coproduction processes are considered.

$CO_2$ 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 $CO_2$ to carbon monoxide and combining it with hydrogen results in syngas.[61] Syngas can also be produced by $CO_2$ reforming of hydrocarbons and by coelectrolysis of $CO_2$ and $H_2O$.[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] $CO_2$ conversion to methanol is usually done by its catalytic hydrogenation. $Cu/ZnO/Al_2O_3$ catalyst is usually used[64] 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 $CO_2$ 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 $CO_2$ emissions. Methane is particularly used as a fuel, and as a reactant in rubber manufacturing as well as in carbon black production.[66] $CO_2$ 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 $CO_2$ has the significant potential to reduce $CO_2$ 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 $CO_2$ emissions by ethanol burning will be zero. Ethanol has the potential to be used as an environment friendly fossil alternative fuel but $CO_2$ 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 $CO_2$ mitigation. $CO_2$ can also be converted to formic acid by its electrochemical reduction in which coelectrolysis of $CO_2$ and $H_2O$ results in methanol production (which is then converted to formic acid).[70] Currently, production of formic acid from $CO_2$ is not a well-developed process and special focus is needed on development of this process to take full advantage of its $CO_2$ 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 $CO_2$ 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] $CO_2$-based production of DMC is recently practiced due to its $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ are mature technologies while some are under development such as production of ethylene carbonate, propylene carbonate, ethane, and so fortg 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$. Further details on the current role of PSE and its future prospective in $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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

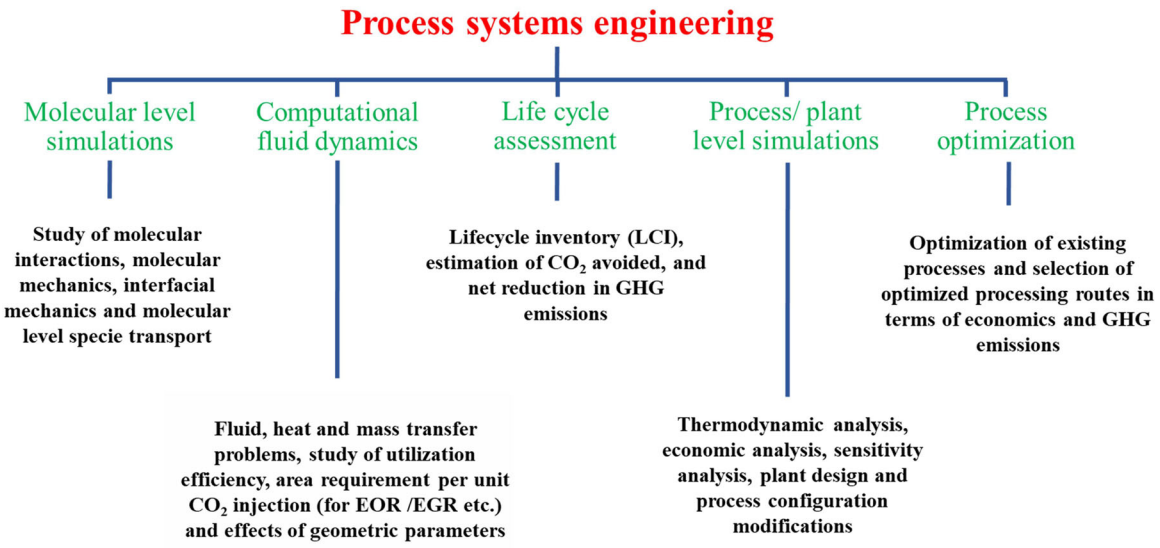


FIGURE 3 Use of PSE in development of $CO_2$ utilization processes

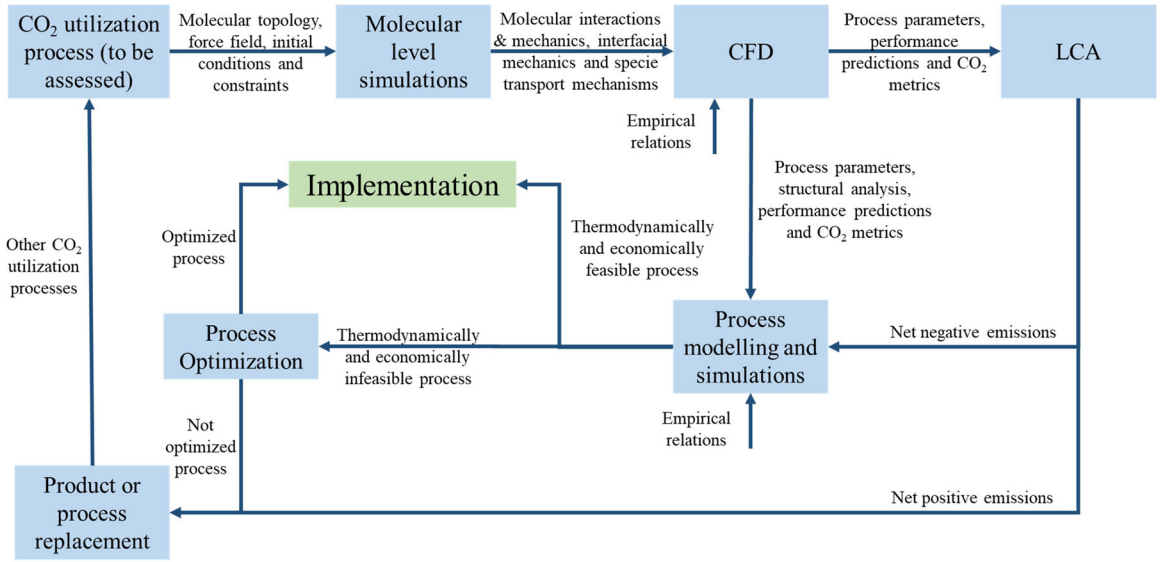


FIGURE 4 Framework to assess $CO_2$ utilization processes using PSE tools and techniques

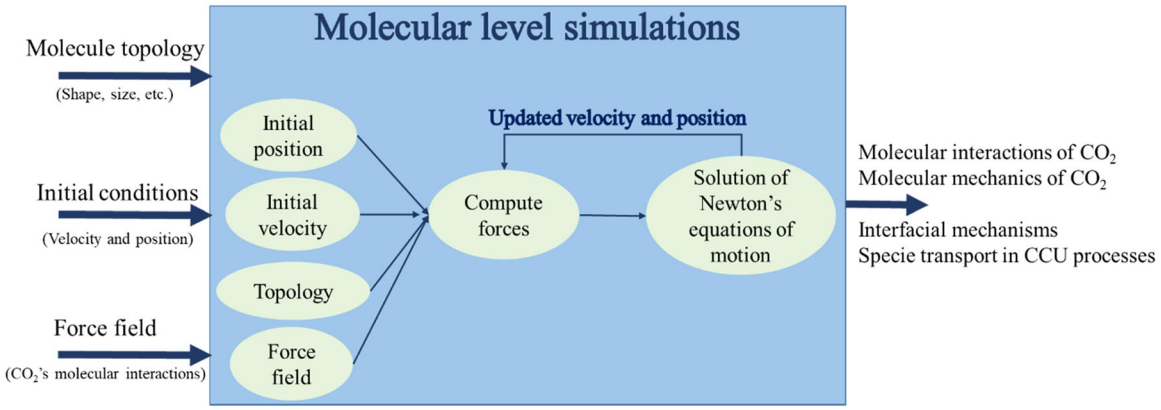


FIGURE 5 Schematics of a molecular level study

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 $CO_2$ 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 $CO_2$ 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 $CO_2$ and $H_2O$ 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 $CO_2$, but presence of water hindered the diffusion of both $CO_2$ and IL. The molecular interactions associated with incorporation of $CO_2$ in montmorillonite clay using MD simulations were studied[77] 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 ZrO2 | Catalytic activity of $Cu/ZrO_2$ catalyst in $CH_3OH$ synthesis from $CO_2$ | VASP | n/a | [88] |

TABLE 3 (Continued)

| Sr. # | Utilization/ Sequestration/ Capture | Process | Performance parameter | Parameters studied | Software used | Validation | Reference |
|---|---|---|---|---|---|---|---|
| 14 | Utilization | 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] |
| 15 | Utilization | 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] |
| 16 | Utilization | Hydrogenation of $CO_2$ | $CO_2$ adsorption, dissociation and hydorgenation over Fe facets (100), (110), (111) and (211) | Catalytic properties of different Fe facets in hydrogenation of $CO_2$ | VASP | n/a | [91] |
| 17 | Utilization | 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 $CO_2$ with amines was investigated. Quantum and molecular mechanics (QM/MM) simulations were performed using the method of umbrella-sampling[93] 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 $CO_2$ and translocation of hydrocarbons in shale inorganic nanopores.[81] Low $CO_2$ injection rate accompanying large injection volume showed amplification in oil recovery. In another study, $CO_2/N_2$ slug injection for EOR was investigated using MD simulations.[82] $CO_2$'s swelling effect and $N_2$'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 $CO_2$, $N_2$ and flue gas, separately. In another study, phase behavior of $CO_2$ EOR was simulated using MD simulations[83] and reported high affinity of $CO_2$ 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 $CO_2$ adsorption. However, in case of $CO_2$ mixed with methane, the adsorption of $CO_2$ dominated in the presence of water. Competitive adsorption behavior of $CO_2/CH_4$ 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, $CH_4$, and $CO_2$ system was examined using MD simulations.[84] Swelling of kerogen was observed on sorption of $CO_2$ and $CH_4$; however, swelling caused by $CO_2$ was less intense than that caused by $CH_4$. This would lead to an increase in recovery of gas from shale. Moreover, $CO_2$ was observed to be strongly bound to kerogen as compared to $CH_4$ providing a mean to sequester its large volumes.

Molecular level studies can also be used to estimate the adsorption capacity of $CO_2$ on different surfaces. The selective adsorption of $CO_2$ from $N_2$ 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 $CO_2/H_2O$, $CO_2/CH_4$ and $CO_2/N_2$

using molecular simulations were presented.[80] Polarity was induced in the surface which increased the selectivity of $CO_2$ over $CH_4$ from 2 to greater than 5 and the selectivity of $CO_2$ over $N_2$ was increased from 5 to 20. However, selectivity of $H_2O$ was greater than $CO_2$ in carbon-based system containing hydrogen.

As already discussed, most of the reactions of $CO_2$ are carried over catalysts. Interaction of $CO_2$ with catalyst surfaces and mechanism of $CO_2$ conversion can be studied on micro scale using the molecular level studies. Reaction mechanism of $CO_2$ hydrogenation to $CH_3OH$ using $Cu/TiO_2$ and $Cu/ZrO_2$ catalysts was studied on molecular level by combining density functional theory (DFT) and kinetic Monte Carlo (KMC) simulations with in-situ experimental measurements.[87] $ZrO_2$ was found to be more effective than $TiO_2$ in terms of both catalyst activity (synergy between reduced $Zr^{3+}$ and Cu sites) and $CH_3OH$ selectivity (for 100 ml/min solution flowrate, 28.3% in case of $ZrO_2$ and 19.1% for $TiO_2$). In another study, activity of $Cu/ZrO_2$ catalyst in $CH_3OH$ synthesis from $CO_2$ was studied using quantum chemical calculations.[88] Conditions of catalyst preparation significantly impacted the Cu dispersion, its electronic state and polymorphic phases of $ZrO_2$ (tetragonal and monoclinic phases). Catalytic activity for $CH_3OH$ synthesis increased with increasing t-$ZrO_2$ (tetragonal phase) content.

DFT and microkinetic studies were used to investigate the $CO_2$ 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 $CO_2$ hydrogenation to formate, carboxyl, and formic acid on Ni(110) was carried out.[90] It was presented that $CO_2$ 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 $CO_2$ to formic acid could take place on Ni(110) catalyst only in the presence of subsurface H.

Investigations of facets effect on $CO_2$ 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 $CO_2$ conversion pathway. $CO_2$ 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–$CO_2$ interactions on molecular level may help identifying the suitable solvent for $CO_2$ 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, $CO_2$ 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 $CO_2$ sequestration, simultaneously increasing the production of fuels. Molecular-level investigations can give insights to chemical utilization processes of $CO_2$. Limiting mechanisms, barriers and molecular interactions in $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization are limited and most of the available literature covers carbon capture.[95–100] A few CFD studies are available on $CO_2$ 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 $CO_2$ 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 ($CO_2$/$H_2O$) 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] |

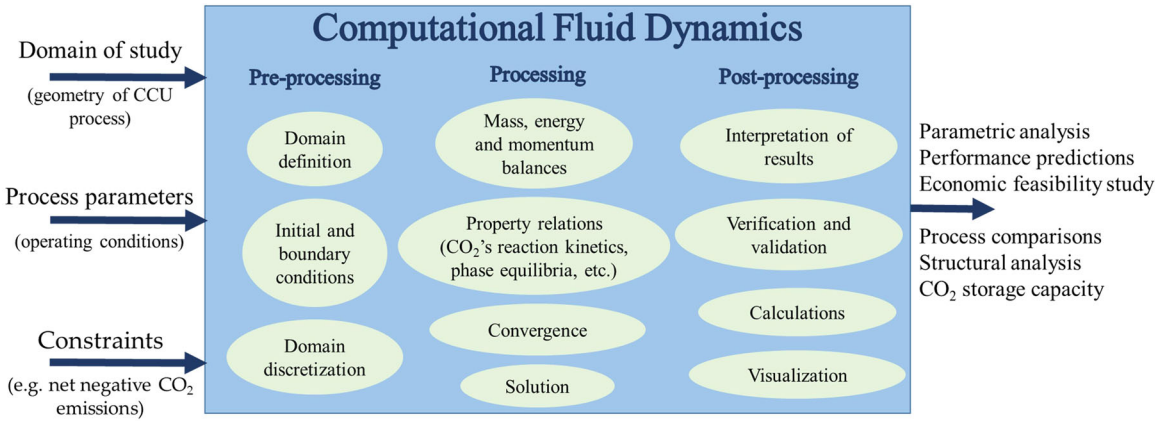


**FIGURE 6** Schematics of a computational fluid dynamics study

The model of a chemical looping combustion (CLC) fuel reactor to find the optimal operating conditions was developed[95] 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 $CO_2$ reactor using CPFD'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 $CO_2$ 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 $CO_2$ 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 $CO_2$ sequestration potential, economic feasibility, and process effectiveness. $CO_2$ storage facility in New Albany shale using EGR was investigated.[101] The well was simulated using GEM simulator. Impacts of $CO_2$ injection, storage capacity, and effectiveness of EGR system were studied. The well was found to have the capacity to accommodate $4 \times 10^4$ metric tons of $CO_2$, injected within 5 years. In another study, a natural gas reservoir using $CO_2$ as working fluid for EGR was simulated[102] using a 3D model. The results showed an increased gas recovery along with sequestration of large volume of $CO_2$. A simulation tool was developed to simulate $CO_2$ injection in the western section of Farnsworth Unit, Texas[103] 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 $CO_2$. These simulations could help in understanding the mechanisms of $CO_2$ 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 $CO_2$. This study could be applied to other similar systems, for example, EGS, EGR and enhanced water recovery. Numerical simulations of $CO_2$ and water injection for EGS were carried out[105] and substantially higher heat extraction was found for $CO_2$ as compared to water. A steady-state solver was developed to study reactions and heat transfer of $CO_2$ 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 $CO_2$ methanation process.

$CO_2$ 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. $H_2$ 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 $CH_4$) 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 $CO_2$ hydrogenation to $CH_3OH$ over $Cu/ZnO/Al_2O_3$ 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 $CO_2$ 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 $CO_2$ storage capacities of EOR and EGR wells. CFD studies are a decent tool to model $CO_2$ 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 $CO_2$ 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 LCA[112]: (1) goal and scope, (2) inventory analysis, (3) impact assessment, and (4) interpretation. Selection of $CO_2$ utilization processes is a critical decision. One of the important questions that must be addressed while $CO_2$ utilization process selection is "whether or not the process will give net reduction in GHG emissions?". Reduction in environmental impacts by implementation of $CO_2$ utilization processes cannot be taken for granted and the environmental feasibility should be evaluated. LCA is the broadly accepted way to assess $CO_2$ utilization processes among industrialists and researchers.[113] However, LCA studies on $CO_2$ utilization processes are limited to a few processes only, including production of DMC, methanol, polymers, formic acid, carbon monoxide, methane, and $MgCO_3$.

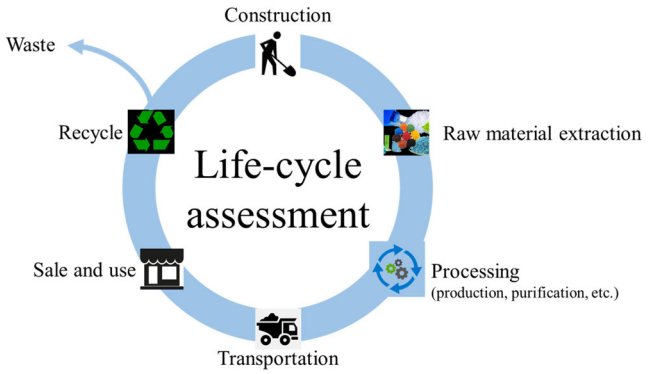


FIGURE 7 Stages of a typical LCA study. *Source*: Modified from Brusseau,[110] with permission from publisher.

The $CO_2$ footprints of mineral carbonation ($MgCO_3$ production) were evaluated by considering four projected scenarios.[114] In the first two scenarios, $CO_2$ was captured from natural gas combined cycle (NGCC) power plant by amine-based PCCC and in other two scenarios direct mineralization of $CO_2$ was employed. Ecoinvent and GaBi life cycle engineering packages were used for analysis and the two scenarios with direct $CO_2$ mineralization were found to be superior in terms of $CO_2$ avoided. In another study, a coal-fired power plant with utilization of captured $CO_2$ to $MgCO_3$ was assessed using Aspen Plus© and Sima Pro©[115] and mineralization of 1 ton $CO_2$ resulted in 483 kg $CO_2$ avoided. The conventional route (from phosgene) and $CO_2$-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 ($CO_2$ based) for DMC production demonstrated low impacts on the environment.

A framework to environmentally assess CCU processes using LCA was developed in which $CO_2$ 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 $CO_2$-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 $CO_2$ was analyzed.[119] The results were compared with conventional formic acid production and CCS route. The CCS route provided more reduction in $CO_2$ 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 $CO_2$-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 $CO_2$ emissions from the power plant when captured $CO_2$ was used for EOR. In another study, net lifecycle $CO_2$ emissions from EOR process were investigated.[122] It was found that for 1 ton of $CO_2$ sequestered, 3.7−4.7 tons of $CO_2$ were released. Several studies[123–127] are available on LCA of $CO_2$ 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 $CO_2$ utilization processes was proposed[128] 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 $CO_2$ 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 $CO_2$ capture is available but the main focus of this section will be on $CO_2$ utilization. This section is divided into two subsections: (1) a very brief summary of process simulations-related contributions to $CO_2$ capture, (2) a critical review of process-level simulations for $CO_2$ 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 $CH_3OH$ & 1,273 kWh; ton $CO_2$-eq/ ton polym. | 59% less emissions ($CH_3O$ 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 | $8.94 \times 10^{10}$ 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 $CO_2$ utilization is gaining importance to mitigate climate change issues. Several researchers have simulated $CO_2$ 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 $CO_2$ utilization process. Plant design analysis involves the detailed evaluation of equipment sizing, and process material and energy flows.

A number of $CO_2$ utilization processes have been thermodynamically analyzed by various authors. The effect of different operating conditions was evaluated for gasification of carbonaceous feedstock using $CO_2$ and a mixture of $CO_2$ 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 $CO_2$ conversion. The thermodynamic analysis of utilization of $CO_2$ from combined heat and power (CHP) system based on cogasification of coal and biomass was presented.[148] Optimal supply ratio of $CO_2$ (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 $CO_2$

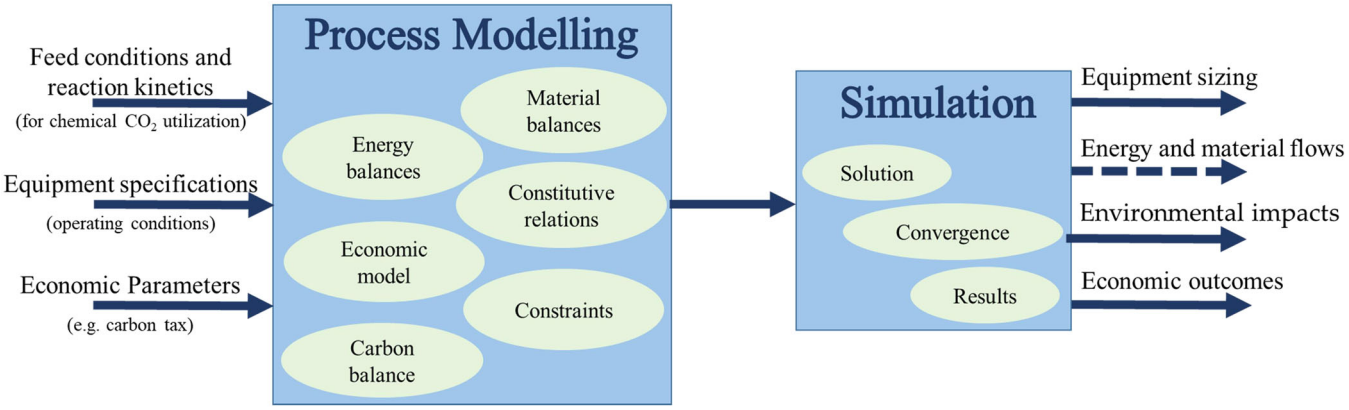


FIGURE 8 Schematics of process modeling and simulation studies

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 $CO_2$. 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 used[150] to evaluate the optimal conditions of $CO_2$ hydrogenation. The use of membrane reactor without recycle, operating at 200°C and introduction of 10% CO in feed was suggested. The resulting $CO_2$ 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 $CO_2$ to syngas was investigated.[151] Various raw material ratios (methane to $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 ($CO_2$ injection, oil production, and $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization routes for DMC production was performed.[155] Four routes of $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ in feed (i.e., 10%, 20% and 50% of total $CO_2$ 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 $CO_2$ and hydrogen was carried out[158] 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 $CO_2$ captured from cement plant was presented using thermo-economic analysis. The process was found to have the ability to treat 2475 ton $CO_2$/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 $CO_2$ 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 $CO_2$ utilization for the production of DME via dry reforming of methane into syngas was performed using Aspen Plus and hybrid LCA.[159] Solvent-based $CO_2$ capture was employed to capture its emissions from a hydrogen production unit in a refinery. It was found that 94% of the total captured $CO_2$ been utilized for DME production and only 9% of $CO_2$ was avoided due to direct $CO_2$ 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 $CO_2$ and $H_2$ 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 $CO_2$ captured from industrial processes to urea and methanol was simulated[26] 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 $CO_2$ per ton of $CO_2$ consumed (net negative $CO_2$ emissions) in case of urea and 6.8 ton $CO_2$ per ton of $CO_2$ consumed (net $CO_2$ 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 $CO_2$ abatement was identified.[162]

Methanol production process by $CO_2$ 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 $CO_2$ capture by chemical absorption, which substantially reduced the capture impact on the power plant economics. Large reduction in $CO_2$ emissions was possible if carbon-free hydrogen source was chosen. The process was modified[65] by optimizing the compression network.

The integration of captured $CO_2$ (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 $CO_2$ 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 $CO_2$ 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 $CH_4$ and $CO_2$, thermal energy intensity, methanol productivity, and $CO_2$ uptake flexibility. The proposed methanol production configuration was found

to consume natural gas with up to 23.2% (mole) $CO_2$. Furthermore, the highest $CO_2$ abatement intensity (45.5%) was found by EGR and using geo-sequestration.

A complex electrochemical reduction model of $CO_2$ to formic acid or formate[165] 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 $CO_2$ 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 Plus[167] 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 $CO_2$.

More sustainable routes to abate atmospheric $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization processes are under consideration to increase the net profit or to decrease the net emissions. Most of the $CO_2$ utilization processes (e.g., methanol production by $CO_2$ 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 $CO_2$ 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). $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization efficiency of 96% was found with 25 or more biofilm reactors connected in series. The concentrated $CO_2$ stream with plug flow behavior was identified to be a critical factor for high $CO_2$ utilization and biomass production.

Mixed integer nonlinear programming (MINLP)-based synthesis model was formulated[175] to maximize the $CO_2$

**TABLE 6** Modeling and simulation of $CO_2$ 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, terrified 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 GEOPHIRES | [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, $CH_3OH$ 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] |

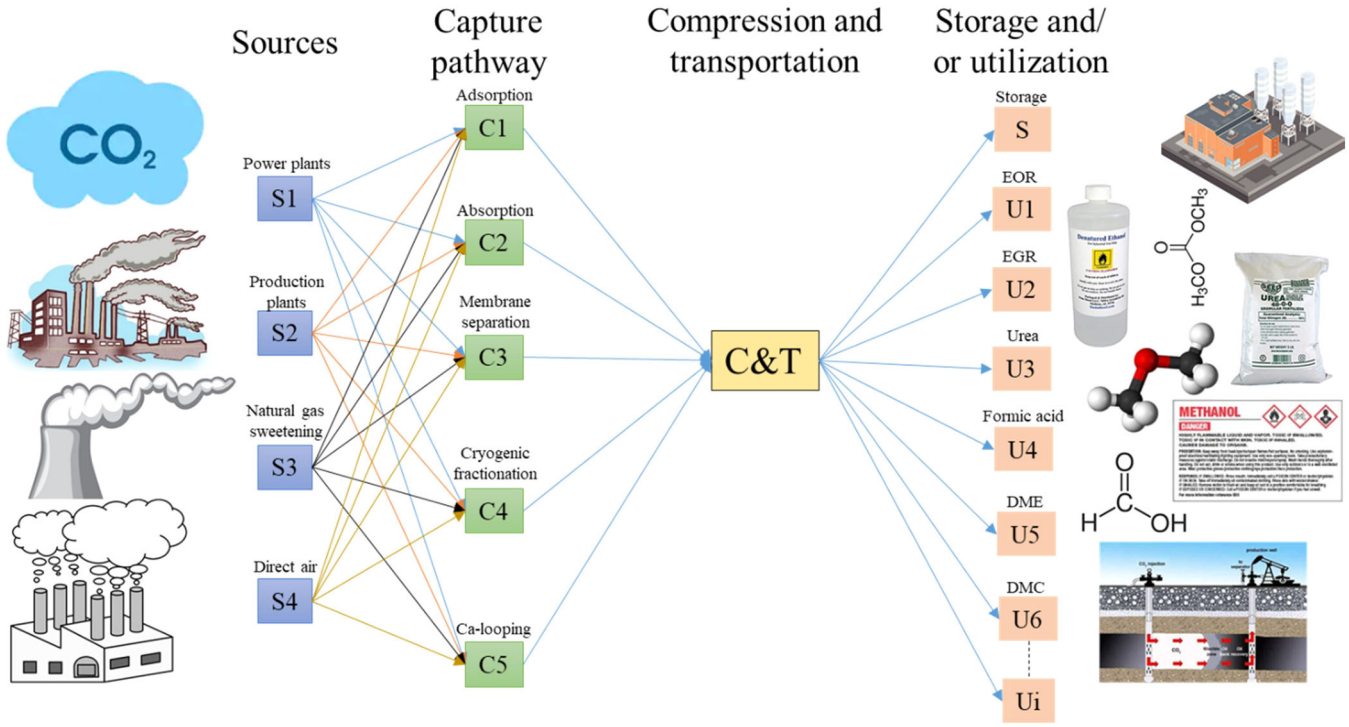


FIGURE 9 A general superstructure of CCU

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-TAC[3] 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ utilization to get economic benefits along with $CO_2$ mitigation. In this way, the captured $CO_2$ can be utilized to produce valuable end products. Being a highly stable molecule, $CO_2$ requires elevated conditions of temperature and pressure for its conversion which needs substantial amounts of energy. This energy demand for $CO_2$ utilization can be reduced by using special catalysts. The current status and challenges for $CO_2$ utilization are presented in this article from thermodynamic, economic and environmental point of view. The advancements and improvements in $CO_2$ utilization have been critically analyzed using the quantitative and qualitative information obtained from experimental and computational studies. The selection of a specific $CO_2$ 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 $CO_2$ utilization.

- Integration of $CO_2$ 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 $CO_2$ (except EGS) are considered mature technologies and can sequester large volumes of $CO_2$ for long period of time. However, carbonated beverages, fire extinguishers and dry ice do not actually sequester $CO_2$ as ultimate fate of the gas utilized by these processes is its emission back to environment.
- Methane has the highest potential to mitigate $CO_2$. However, currently most of the global methane is extracted from natural gas wells. As natural gas reserves are depleting continuously, the future of $CO_2$ utilization for methane production is bright. The $CO_2$ 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 $CO_2$.

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 | Actetic 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 $MgCO_3$ production, DMC production, methanol production, EOR and biodiesel production from microalgae as the environmentally sustainable options among $CO_2$ utilization processes while formic acid production through $CO_2$ 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 $CO_2$ 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.
- $CO_2$ utilization is a vast field which is under exploration in wide areas from multiple fronts for improving the economic and environmental impacts.

$CO_2$ utilization provides an attractive opportunity for reducing global warming potential of several industrial sectors. $CO_2$ utilization projects should be implemented on large scale for economic benefits concurrently reducing $CO_2$ 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 $CO_2$ utilization processes to assess and forecast the overall potential of $CO_2$ utilization and its economic and environmental feasibility.
- More focus should be given to the development of novel catalysts for conversion of $CO_2$ to reduce the high energy requirements, for example, considering the example of methane production which have significant $CO_2$ 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 $CO_2$ 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 $CO_2$ as working fluid should be optimized to improve its economics.
- Hydrogen is used as a raw material in many chemical $CO_2$ utilization processes including methanol, ethanol, DME, DMC and methane production. Its economics must be improved to improve the overall economics of $CO_2$ utilization especially by utilizing renewable energy.

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