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To cite this article: Shu-Yuan Pan, Pen-Chi Chiang, Weibin Pan & Hyunook Kim (2018) Advances in state-of-art valorization technologies for captured CO₂ toward sustainable carbon cycle, *Critical Reviews in Environmental Science and Technology*, 48:5, 471-534, DOI: [10.1080/10643389.2018.1469943](https://doi.org/10.1080/10643389.2018.1469943)

To link to this article: <https://doi.org/10.1080/10643389.2018.1469943>



Published online: 29 May 2018.



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Advances in state-of-art valorization technologies for captured CO₂ toward sustainable carbon cycle

Shu-Yuan Pan^a, Pen-Chi Chiang^{a,b}, Weibin Pan^c, and Hyunook Kim^d

^aCarbon Cycle Research Center, National Taiwan University, Taipei, Taiwan (ROC); ^bGraduate Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan (ROC); ^cSchool of Environmental Science and Engineering, South China University of Technology, Guangzhou, China; ^dDepartment of Energy and Environmental System Engineering, University of Seoul, Seoul, South Korea

ABSTRACT



Valorization of captured CO₂ is an important but challenging topic since CO₂ is a stable and relatively inert compound. Nonetheless, CO₂ valorization technologies should be sought after, because they can offer an opportunity for the sustainable carbon cycle towards a circular economy by creating value-added products and generate revenues from CO₂. This paper provides an overview of state-of-the-art valorization technologies for captured CO₂, including (1) supercritical CO₂ as a reactive solvent, (2) mineralization of CO₂ as inorganic carbonates, (3) catalytic reduction of CO₂ into organic fuel for transport, (4) transformation of CO₂ to value-added chemicals, and (5) biological CO₂ utilization. The principles and application, in terms of CO₂ conversion performance and environmental benefits of each technology, are reviewed in detail. In addition, the perspectives and prospects of CO₂ valorization technologies as a portfolio solution are provided to achieve the effective CO₂ reduction while minimizing social and economic costs in the near future.

KEYWORDS

Bio-chemicals; catalyst; dimethyl carbonates; hydrogenation; microalgae; mineralization; supercritical; sustainable organic fuel for transport; water electrolysis

1. Introduction

Human activities led to an imbalance in the global carbon cycle since the rate of CO₂ release mainly due to the burning of fossil fuels and cement production, exceeds that of CO₂ uptake and sequestration (Farrelly et al., 2013). In response to Paris Agreement in 2015, an effective control of CO₂ emission is necessary to keep the global atmospheric CO₂ concentration below 550 ppm over the next 100 years (Fernandez Bertos et al., 2004). The concentration of CO₂ in the atmosphere increases at a rate of 4.2 Gt-C/year (Scholes et al., 2009). However, it has been predicted that fossil fuels will remain the worldwide-dominant source of energy at least for the next 20 years (Aresta, 2010b). Several imperative strategies on CO₂

CONTACT Hyunook Kim  h_kim@uos.ac.kr  Department of Energy and Environmental System Engineering, University of Seoul, 163 Seoulsiripdae-ro, Jeonnong 2(i)-dong, Dongdaemun-gu, Seoul, South Korea.

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mitigation have been proposed to combat the aforementioned challenges. One of them is widespread deployment of valorization technologies for captured CO₂. CO₂ valorization technologies would offer the potential of reducing annual CO₂ emissions by at least 3.7 Gt, which is about 10% of the world's current annual emissions (CSLF, 2011; Pan et al., 2015b). Meanwhile, value-added products can create green jobs and economic benefits and help offset the implementation cost by substitution of chemicals such as chlorofluorocarbons (Aresta, 2010b).

CO₂ molecule is a thermodynamically stable compound. Figure 1 shows the approximate chemical energy (Gibbs free energy) of C1 species and hydrogen relative to CO₂. The diluted or concentrated CO₂ can be directly utilized or converted into carbon-based materials such as hydrocarbon fuels and chemicals. CO₂ conversion can be realized by either reduction reaction (i.e., to a negative-going oxidation state) (Wang et al., 2014) or mineralization (i.e., to a lower Gibbs free energy) (Duan et al., 2014) since CO₂ has the highest oxidation state (4+) among all carbon-bearing compounds. For instance, CO₂ mineralization using natural ores and/or solid wastes (Olivares-Marín and Maroto-Valer, 2012) and biological methods such as microalgae and enzyme-based processes (Klinthong et al., 2015) are related to direct CO₂ utilization and conversion since the physico-chemical property of CO₂ changes after process. Otherwise, CO₂ reductive conversion typically goes through a catalytic process with typically additional energy input (e.g., renewable energy source).

CO₂ valorization technologies can offer a unique opportunity for sustainable carbon cycle towards a circular economy. Extensive efforts have been carried out to enhance the CO₂ conversion efficiency and product selectivity under various novel processes. Figure 2 shows the roadmap of valorization technologies for captured CO₂. CO₂ valorization can be achieved by either (i) direct use of

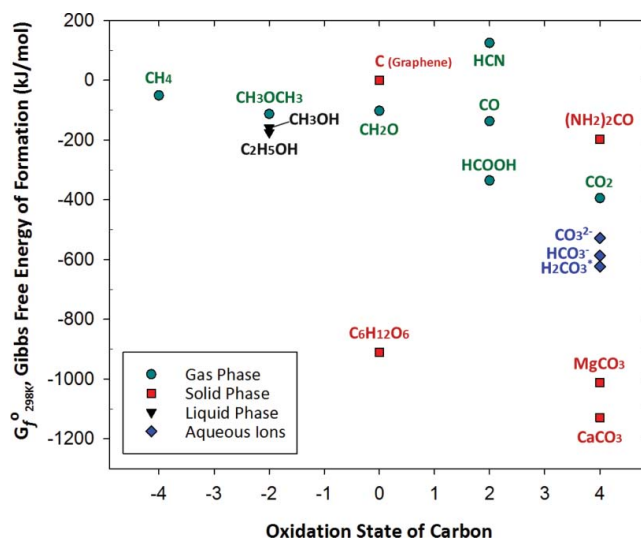


Figure 1. Approximate chemical energy (Gibbs free energy) of C1 species and hydrogen relative to CO₂.

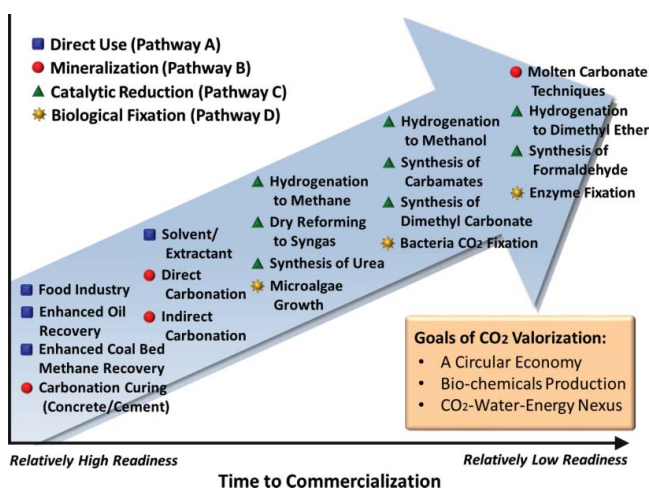


Figure 2. Roadmap of valorization technologies for captured CO₂. Aresta; et al., 2014; Chery et al. 2015; Sanna et al., 2014.

concentrated CO₂ (i.e., Pathway A (use as a reactive solvent) (Huang and Tan, 2014) in Figure 2), or (ii) CO₂ conversion into chemicals and/or fuels (i.e., Pathways B (mineralization) (Aresta et al., 2014; Chery et al., 2015; Sanna et al., 2014), C (catalytic reduction), and D (biological fixation) in Figure 2). The goal of CO₂ valorization is to use CO₂ as a feedstock to produce bio-fuels and/or bio-chemicals towards a circular economy. Meanwhile, these technologies should be able to address the issues of water and energy nexus since production of freshwater or energy requires work-inputs, which would result in additional CO₂ emissions.

To facilitate the development of a sustainable carbon cycle, this paper provides an overview of state-of-the-art CO₂ valorization technologies, including (1) use of supercritical CO₂ (sc-CO₂) as a reactive solvent, (2) mineralization of CO₂ as inorganic carbonates, (3) catalytic reduction of CO₂ into organic fuel for transport, (4) transformation of CO₂ to value-added chemicals, and (5) biological CO₂ utilization technology. The advances in each technology and environmental benefits are comprehensively reviewed. The perspectives and prospects of each CO₂ valorization technology as a portfolio solution are also provided to achieve effective CO₂ reduction while minimizing social and economic costs.

2. Supercritical CO₂ as a reactive solvent

Supercritical CO₂, considered as a green solvent system, can be formed when CO₂ is held at or above its critical temperature (31.1°C) and critical pressure (~7.39 MPa). sc-CO₂ can be applied in many different fields of interest, for examples, as a swelling agent (Kegl et al., 2017), working fluid in Rankine cycles (Li et al., 2016), fracturing fluid (Cui et al., 2016; Middleton et al., 2015), extractant (Li et al., 2014b; Pan et al., 2012a; Taher et al., 2014), pasteurizing agent of bioactive compounds in food and medicine (Jermann et al., 2015), homogeneous and

heterogeneous catalysis (Galia and Filardo 2010; Hu et al., 2016; Koeken et al., 2011), polymer synthesis and modification (Du et al., 2009; Haldorai et al., 2012), and bio-catalysis (Hobbs and Thomas, 2007). From an engineer's point of view, sc-CO₂ would be a good solvent for amorphous fluorinated polymers, silicones and poly(ether-carbonate) copolymers but might be a marginal one for hydrogenated polymers (Triolo et al., 2002). From the economic aspect, Rosa and Meireles (2005) estimated the costs of manufacturing the solvent and compared it with its corresponding price in the market. In the commercial adoption of supercritical fluid extraction, the manufacturing costs can be determined by considering (i) direct costs such as raw materials, operational labor, and utilities, (ii) fixed costs such as investment, and (iii) operation and maintenance (del Valle, 2015). In this section, the applications of sc-CO₂ in extraction as well as in polymer synthesis and modification are illustrated and reviewed.

2.1. Extraction of valuable components from microalgae

Extraction using sc-CO₂ offers immediate advantages over other extraction techniques using a conventional solvent: (i) the process is flexible with the possibility of continuous modulation of the solvent power/selectivity of the supercritical fluids, (ii) it eliminates polluting organic solvents, and (iii) expensive postprocessing of extracts for solvent elimination is not required (Reverchon and De Marco, 2006). Nowadays, sc-CO₂ extraction of molecules of interest from microalgae biomass is a subject of great interest documented (Mouahid et al., 2013; Yen et al., 2015b). Numerous components in microalgae have highly valuable products, such as total lipid (Li et al., 2014b), long chain fatty acids (e.g., eicosapentaenoic acid and docosahexaenoic acid) (Li et al., 2014b), and pigments (e.g., astaxanthin (Pan et al., 2012a), lutein (Yen et al., 2011), α -linolenic (Solana et al., 2014), and β -carotene) (Nobre et al., 2013). The lipid content of microalgae typically ranges from 20% to 50% of its dry weight with a potential up to 80%, which can be utilized for biofuel application. Similarly, astaxanthin and lutein are typical carotenoid members, which are widely used as food additives and nutritional supplements (Yen et al., 2015b). Daily intake of these pigment, is recommended since human body cannot synthesize them. For instance, lutein is naturally synthesized by plants in the form of fatty-acid esters with one or two fatty acids bound to two hydroxyl groups. It was noted that nonpolar sc-CO₂ would be suitable for extraction of neutral lipids such as triglycerides (Jeevan Kumar et al., 2017).

Table 1 presents the different extraction methods for valuable compounds from microalgae biomass. The extraction efficiency of a supercritical fluid process depends on intrinsic factors (such as temperature, pressure and duration) and extrinsic ones (such as sample matrix characteristics and interactions of sc-CO₂ with target compounds). The results indicate that the pigment recovery using sc-CO₂ could be over 80% under a specific condition, suggesting that sc-CO₂ fluid is a promising solvent for the separation of pigment in the microalgae. In addition, it

Table 1. Different extraction methods for valuable compounds from microalgae biomass.

Solvent	Biomass ^a	Compound of interest	Extractant formula	Press. (MPa)	Temp (°C)	Extraction time (hours)	Performance	Reference
CHCl ₃	Seeds (<i>E. virescens</i>)	Total fatty acid ^b	CHCl ₃ /MeOH = 2:1; 0.88% KCl agitation/centrifuge	n.r.	n.r.	2	Amt: 109.9 ± 9.3 mg/g of dry weight	(Cequier-Sanchez et al., 2008)
CH ₂ Cl ₂	Seeds (<i>E. virescens</i>)	Total fatty acid ^b	CH ₂ Cl ₂ /MeOH = 2:1; 0.88% KCl agitation/centrifuge	n.r.	n.r.	2	Amt: 107.5 ± 9.0 mg/g of dry weight	(Cequier-Sanchez et al., 2008)
sc-CO ₂	Microalgae	Total fatty acid ^b	CO ₂ (no modifier)	15	40	12	mean% of dry weight: 10.00 ± 0.27	(Li et al., 2014b)
sc-CO ₂	Microalgae (<i>Scenedesmus</i> sp.)	Total lipid	CO ₂ (no modifier)	50	53	1.5	Yield ^c = 7.34%	(Taher et al., 2014)
sc-CO ₂	Microalgae (<i>N. salina</i>)	Total lipid	CO ₂ + 5% EtOH	30	45	1.5	Yield ^c = 30.4%	(Solana et al., 2014)
sc-CO ₂	Microalgae (<i>Nannochloropsis</i> sp.)	Total lipid	CO ₂ + 5% EtOH	30	40	1	Yield ^c = 33%	(Nobre et al., 2013)
sc-CO ₂	Microalgae (<i>Nannochloropsis</i> sp.)	Total lipid	CO ₂ + 20% EtOH	30	40	1	Yield ^c = 45%	(Nobre et al., 2013)
sc-CO ₂	Microalgae (<i>H. pluvialis</i>)	Astaxanthin	CO ₂ + 20% EtOH	45	50	0.33	Recovery = 73.9%	(Pan et al., 2012a)
sc-CO ₂	Microalgae (<i>H. pluvialis</i>)	Astaxanthin	CO ₂ + 2.3 mL EtOH/g sample	43.5	65	3.5	Recovery = 87.4%	(Wang et al., 2012)
sc-CO ₂	Microalgae (<i>H. pluvialis</i>)	Astaxanthin	CO ₂ + 1.3% EtOH	20	55	2	Recovery = 82.3%	(Reyes et al., 2014)
sc-CO ₂	Microalgae (<i>C. vulgaris</i>)	Lutein	CO ₂ + 10% EtOH	40	40	2	Recovery = 52.9%	(Ruen-ngam et al., 2012)

^a*E. virescens* (*Echium virescens*); *N. salina* (*Nannochloropsis salina*); *H. pluvialis* (*Haematococcus pluvialis*); *C. vulgaris* (*Chlorella vulgaris*).

^bFatty acid includes saturated fatty acid, monounsaturated, and polyunsaturated.

^cThe amount of extracted oil divided by the amount of biomass applied.

was observed that using a polar compound like ethanol as a cosolvent could increase the solubility of carotenoids in sc-CO₂. In the case of astaxanthin extraction from *Haematococcus pluvialis*, Reyes et al. (2014) found that ethanol content in sc-CO₂ would affect yield, astaxanthin content and antioxidant activity more than pressure and temperature. The results indicate that the astaxanthin recovery using sc-CO₂ could be over 87% (Wang et al., 2012). However, one limitation is that sc-CO₂ would reduce the extraction efficiency of a polar cosolvent (Pan et al., 2015c). In addition, sc-CO₂ technology for extraction of valuable components from microalgae biomass still suffers from high equipment cost and operating cost (Yen et al., 2015b).

2.2. Polymer synthesis and modification

Supercritical fluids such as sc-CO₂ can be used in polymer synthesis, modification and processing. It can change the rheological and thermo-physical properties of a polymer such as the glass transition and the melting temperature when it is exposed to sc-CO₂. Thus, sc-CO₂ was used in numerous applications such as (1) foaming agents for polymers, (2) formation and encapsulation of particles from polymer solutions, (3) extraction of low molecular weight molecules from polymer matrices for purifications, and (4) impregnation of solutes such as drug molecules into polymers (Kegl et al., 2017; Kiran, 2016).

In traditional solvent systems, the polymerization rates could be limited by the local increase in viscosity during the reaction, thereby lowering the mass transfer rate of monomer to reaction site (Galia and Filardo, 2010). Due to low viscosity and high diffusivity of sc-CO₂, the polymerization rate could significantly increase up to the value of monomer conversion. Majority of polymerizations in sc-CO₂ are heterogeneous and involve either precipitation or dispersion since polymers are generally insoluble in sc-CO₂. In addition, as a polymerization medium, sc-CO₂ can be easily removed after polymerization, eliminating the need for an energy-intensive drying process. Therefore, sc-CO₂ is suitably applied for a system that involves heat-sensitive materials such as enzymes, pharmaceuticals, flavors, and highly reactive monomers.

Recently, it was found that hydrothermal modification treatment assisted by sc-CO₂ over polymers could simultaneously result in a physical modification and a hydrolysis reaction in polymers (Alcázar-Alay et al., 2016). Similarly, extrusion assisted by sc-CO₂ can provide rapid mixing and dissolution of CO₂ in the polymer melt, thereby resulting in a decrease of the processing temperature to manufacture of highly porous material (Chauvet et al., 2017). Furthermore, sc-CO₂ can serve as a swelling agent for polymers to impregnate the carrier with desirable substances such as bioactive compounds.

2.3. Summary

The sc-CO₂ technology has the potential of valorizing CO₂ from emission sources, while improving the efficiency and performance of a process and/or reaction such

as extractions, separation, and synthesis and modification of materials (e.g., polymers). For the extraction of valuable compounds, sc-CO₂ is a promising alternative to numerous commercial organic solvents due to its higher selectivity, lower extraction time and more environmentally friendly. At present, however, the sc-CO₂ technology still suffers from high equipment cost and operating cost. The behaviors of supercritical fluids in a process like extraction also still not clearly understood because of the complex interaction between affecting factors and fluid dynamics of supercritical fluids (Wang et al., 2010). The future research should focus on designing the optimized system for supercritical fluid to facilitate the deployment of sc-CO₂ technology.

3. Mineralization of CO₂ as inorganic carbonates

CO₂ mineralization can be accomplished via accelerated carbonation. It has been proven that accelerated carbonation process is thermodynamically practical to enhance the natural weathering (Herzog, 2002; Lackner et al., 1995). In this process, gaseous CO₂ can be mineralized as a thermodynamically stable precipitate, thereby being rarely released after mineralization. CO₂ mineralization via accelerated carbonation can be categorized into three main processes: (1) direct carbonation, which is associated with production of green concretes/cements such as supplementary cementitious materials, (2) indirect carbonation, which is related with production of high value-added chemicals such as precipitated calcium carbonates, and (3) carbonation curing for concrete block and/or cement mortar to enhance their strength and durability. In the following section, the principles and applications of the aforementioned processes are reviewed and discussed.

3.1. Feedstock for CO₂ mineralization via accelerated carbonation

Natural silicate and/or carbonate ores are suitable feedstock for accelerated carbonation due to their high contents of calcium and/or magnesium oxides, such as amphibolite/diopside (Erlund et al., 2016), and serpentine (Veetil et al., 2015). Accelerated carbonation using natural ores could provide high capture capacity and long storage period for anthropogenic CO₂ (Bobicki et al., 2012; Lackner, 2003; Seifritz, 1990). Carbonate minerals are energetically favored to form from the reaction of CO₂ with silicates such as olivine, serpentine and anorthite (Lackner, 2002). It is also known that there is enough natural ores on Earth to sequester all CO₂ emissions from fossil-based sources (Lackner, 2003). However, due to the need for large-scale mining of the natural ores (Kelly et al., 2011), exploring and pretreating materials are costly. Therefore, alkaline solid wastes from industries or coal-fired power plants are getting more attention as an attractive feedstock for accelerated carbonation since they are relatively inexpensive ores. In the meantime, an integrated approach to combining CO₂ valorization with alkaline waste treatment could be simultaneously achieved (Chiang and Pan, 2017d).

Table 2 presents the list of alkaline solid wastes as a suitable feedstock for accelerated carbonation: three examples are iron and steel slags, air pollution control residues, and mining/mineral processing wastes. Different elements such as Pb, Zn, and Cr would be leached out from the solid matrix to the liquid phase (e.g., water environment). These alkaline solid wastes, if added into water, would normally cause solution pH to increase over 10. It is noted that, by introducing flue gas CO₂ as a stabilizing agent, potential environmental impacts of utilizing these solid wastes, with highly alkaline and heavy metal leaching characteristics, can be reduced (Chiang and Pan, 2017f).

Figure 3 shows the normalized CaO(MgO)-SiO₂(Na₂O,K₂O)-Al₂O₃(Fe₂O₃) phase diagram of various types of alkaline wastes for CO₂ mineralization. They are

Table 2. Suitable alkaline solid wastes as a feedstock for accelerated carbonation.

Categories	Types of wastes	Leachable elements	References
Incineration ash	MSWI bottom ash	Pb, Sb, Cu, PAHs	(Arickx et al., 2010; Cornelis et al., 2012; Rendek et al., 2006; Yang et al., 2012)
	MSWI fly ash*	Pb, Cr, Cu, Cd, Ba, Cl, dioxin	
Pulverized fuel ash	Paper sludge	Cr, As, Cu, Mo, Ni, Pb, Se	(Sanna et al., 2012)
	Coal fly ash [†]	Se, Sr, Ba, Cl, Zr, Cr, Ni, Zn	(Liu et al., 2013; Tamilselvi Dananjayan et al., 2016)
	Coal bottom ash (slag)	Mn	(Pyo and Kim, 2017)
	Oil shale ash	S	(Uibu et al., 2011; Velts et al., 2011)
Cement waste	Cement kiln dust	Pb, SO ₄ ²⁻ , Cl-, Ba, Mo	(Abo-El-Enein et al., 2013; Sanna et al., 2012)
	Cement bypass dust		
	Construction and demolition waste		
	Cement/concrete waste		
	Blended hydraulic slag cement		
Air pollution control residue	Cyclone dust*	Pb, Zn, Cd, Cr	(Cappai et al., 2012; Chiang and Pan, 2017b)
	Cloth-bag dust*	Pb, Cr, Cd, Zn, Sr, Cu	(El-Naas et al., 2015; Tian and Jiang, 2012)
Mining and mineral processing waste	Asbestos tailings	Mg, Al	(Chiang and Pan, 2017e; Oskierski et al., 2013)
	Copper tailings (copper-nickel-PEG)	Zn, Cu, Fe, Mn	(Chen et al., 2014; Guo et al., 2013)
	Red mud (Bauxite residue)	Al, Zn, PO ₄ ²⁻ , S	(Molineux et al., 2016)
Iron and steel slag	Blast furnace slag	Si, Al, Fe, Ti, Mn	(Ukwattage et al., 2017)
	Basic oxygen furnace slag	Cr, V	(De Windt et al., 2011)
	Electric arc furnace slag	Cr, Ba, V, Mo	(Mombelli et al., 2016)
	Ladle furnace slag	Fe, Mn, V, Cr, Ba ^a , Mo ^a	(Capobianco et al., 2014; Ibouraadaten et al., 2015; Setién, et al., 2009)
Paper mill waste	Green liquor dreg	Mr, Zn, Ni, Ba, Fe	(Nurmesniemi et al., 2005; Perez-Lopez et al., 2010; Perez-Lopez et al., 2008)
	Paper sludge incineration ash	SO ₄ ²⁻ , Mo, Ba, Cr, Pb	(Jo et al., 2012)
	Lime kiln residues (calcium mud)*	Cr, Mn, Fe	(Qin et al., 2015)

[†]Be usually categorized as a hazardous material.

^aEspecially in the case of argon oxygen decarburization slag.

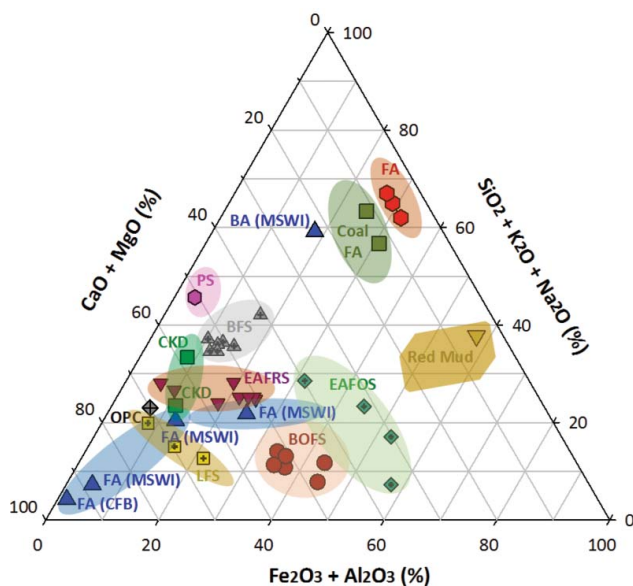


Figure 3. Normalized $\text{CaO}(\text{MgO})\text{-SiO}_2(\text{Na}_2\text{O},\text{K}_2\text{O})\text{-Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$ phase diagram of various types of alkaline waste. FA (fly ash); CKD (cement kiln dust); OPC (ordinary Portland cement); MSWI-FA (municipal solid waste incinerator fly ash); MSWI-BA (municipal solid waste incinerator bottom ash); CFB-FA (circulate fluidized boiler bed fly ash); BFS (blast furnace slag); BOFS (basic oxygen furnace slag); LFS (ladle furnace slag); EAFOS (electric arc furnace oxidizing slag); EAFRS (electric arc furnace reducing slag); PS (phosphorus slag).

chemically unstable with high content of active components, e.g., lime (free- CaO), which can be readily hydrated in the presence of water and react with CO_2 to form carbonates. In general, the Ca- and Mg-bearing compounds mainly contribute to CO_2 fixation capacity, and the Fe_2O_3 content is related to hardness and grindability of a material. Basic oxygen furnace slag and electric arc furnace slag are relatively hard materials due to their high Fe_2O_3 content, i.e., typically 17–38% and even up to 48% (Chiang and Pan, 2017c). On the other hand, if material is used in concrete and cement, the contents of CaO and SiO_2 are primarily related to the hydraulic and pozzolanic properties, respectively. For instance, ordinary Portland cement (OPC) is a hydraulic material, while both blast-furnace slag and fly-ash are, respectively, latent-hydraulic and pozzolanic byproducts (Gruyaert et al., 2013). Conversely, according to the findings reported by Muhmood et al. (2009), electric arc furnace slag is neither hydraulic nor pozzolanic because of its lack of tri-calcium silicates and amorphous SiO_2 content.

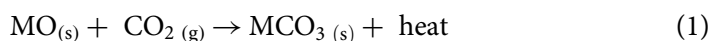
3.2. Direct carbonation with production of green construction materials

CO_2 mineralization via accelerated carbonation involves fixing gaseous CO_2 into thermodynamically stable carbonates. The carbonate products can be utilized as a supplementary cementitious material (SCM) in concrete and/or cement mortar,

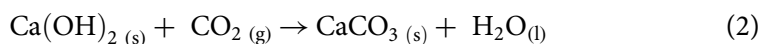
which is a sustainable practice to make the cement industry more environmentally friendly. Thus, this approach can keep globally available alkaline solid wastes out of landfills. Coincidentally to the amount of CO₂ emission and alkaline solid waste production at a single plant, a direct CO₂ mitigation potential of roughly 2% could be achieved if all the solid wastes are on-site utilized to capture the CO₂ emission (Tamilselvi Dananjayan et al., 2016).

3.2.1. Principles and Applications (Process Design)

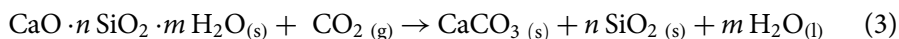
CO₂ can react with divalent metal oxides, such as CaO, MgO, and FeO, to form the corresponding carbonate, as shown in Eq. (1):



Accelerated carbonation is an exothermic reaction, where the amount of heat release depends on the reactive metal (M) and on the material containing this metal oxide (MO). In the case of alkaline solid wastes, residues with a native pH value of greater than 10 typically contain portlandite (Ca(OH)₂), which controls the solubility of calcium ions and the pH of solution (Olajire, 2013). Portlandite can be carbonated with CO₂ via Eq. (2):



Another group of Ca-bearing components that is often present in solid wastes are calcium-silicate-hydrate (C-S-H) phases, such as CaSiO₃ and Ca₂SiO₄ (Pan et al., 2012b; Pan et al., 2015a). The carbonation of C-S-H phases can be described as Eq. (3):



The theoretical CO₂ fixation capacity (ThCO₂, %) of alkaline solid wastes can be estimated based on the chemical compositions of the wastes using the famous Steinour formula (Steinour, 1959). It is assumed that the components of CaO, MgO, NaO, and K₂O would contribute to the carbonation reaction with CO₂. The compositions of each component are applied in terms of a weight percent (%).

$$\begin{aligned} \text{ThCO}_2(\%) = & 0.785(\text{CaO} - 0.7\text{SO}_3 - 0.56\text{CaCO}_3) \\ & + 1.091 \text{MgO} + 2.09 \text{Na}_2\text{O} + 0.93 \text{K}_2\text{O} \quad (4) \end{aligned}$$

Extensive studies have been performed to evaluate the CO₂ fixation capacity of direct carbonation for solid wastes, such as steel slag (Pan et al., 2013b; Santos et al., 2013), fly ash (Tamilselvi Dananjayan et al., 2016), and cement waste (Lee et al., 2016). A challenge in determining the amount of carbonation product exists since the evaluation criteria of carbonate products by conventional

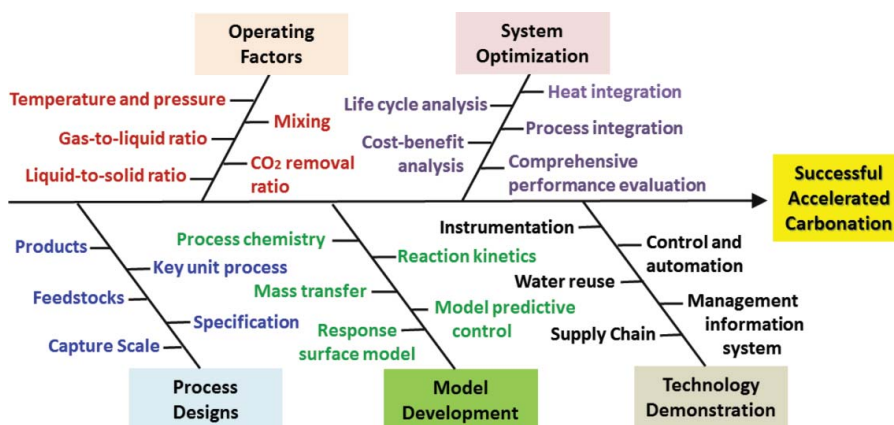


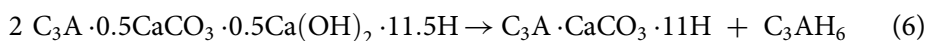
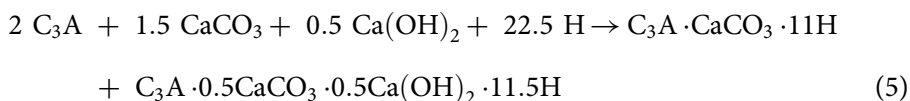
Figure 4. Fishbone of possible influencing factors for accelerated carbonation using alkaline wastes.

thermogravimetric (TG) analysis are quite different among the literature, as well as the various ways to interpret the TG curve. To accurately quantify the CaCO_3 content in solid wastes, Pan et al. (2016d) proposed an integrated thermal analysis by combining the TG analysis results with derivative thermogravimetric, differential thermal analysis, and differential scanning calorimetry.

Figure 4 shows a fishbone diagram of influencing factors for accelerated carbonation using alkaline wastes. To achieve a successful accelerated carbonation, there are five key components which should be critically considered in a large-scale deployment: (1) process designs, (2) operating factors, (3) model development, (4) system optimization, and (5) technology demonstration. For instance, to improve the mass transfer between gas, liquid and solid phases (related to the mixing in operating factors), Pan et al. (2014, 2013a) utilized a rotating packed bed reactor for accelerated carbonation, known as high-gravity carbonation (HiGCarb). In the HiGCarb process, the slurry containing alkaline solid waste and wastewater is fed into the reactor and extracted outward which was motivated by centrifugation. In the meantime, the flue gas enters the reactor from the counter-current direction and moves inward by pressure gradient. A high micro-mixing efficiency between the slurry and gas phases can be obtained, thereby enhancing the CO_2 mass transfer, improving the carbonation conversion and reducing the reaction time (Pan et al., 2015e). Using the process, the 93% carbonation conversion of steel slag could be attained (Chang et al., 2012a). For comparison, typical carbonation conversions of 40–75% are achieved in the slurry (Chang et al., 2012b) and autoclave (Chang et al., 2011) reactors. Recently, on-site HiGCarb demonstrations have been carried out at a steelmaking (Pan et al., 2015d) and a petrochemical (Pan et al., 2016b) industry. The results indicated that, in the case of the steel industry, the energy consumption of the HiGCarb process with a CO_2 removal efficiency of 90% was estimated to be $267 \pm 58 \text{ kWh t-CO}_2^{-1}$ (Pan et al., 2015d).

3.2.2. Product utilization as SCMs in construction engineering

A concrete block comprises of water, cement, coarse and fine aggregates, chemical admixture, and SCM. Studies have been carried out to evaluate the utilization performance of carbonated solid wastes as SCMs in blended cement (Pan et al., 2015d) and a fine aggregate in concrete (Monkman et al., 2009). Normally, the use of SCMs in blended cement may reduce the early-age strength and increase the later-age strength of the concrete, as compared with the use of pure OPC (Caldarone et al., 2005). However, a carbonation product such as CaCO_3 is superior to the original CaO or Ca(OH)_2 in alkaline solid wastes, in terms of physical properties. Since the CaCO_3 is a highly elasticity-resistant material, it can improve early strength of cement mortar. CaCO_3 also could create vacuum within the cement matrix; therefore, liquid cannot easily intrude into the structure to induce corrosion or damage (Chi et al., 2002). Aside from the physical enhancement, the CaCO_3 product may induce the chemical enhancement effect which might be attributed to the hydration of C_3A phase to form stable calcium carboaluminate ($\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}$), as shown in Eq. (5). This reaction could develop a higher mechanical strength in the early stage (Hawkins et al., 2003). In the meantime, the formed by-product ($\text{C}_3\text{A}\cdot 0.5\text{CaCO}_3\cdot 0.5\text{Ca(OH)}_2\cdot 11.5\text{H}$) is relatively unstable and will be continuously converted to calcium carboaluminate after 1 day, as described in Eq. (6).



Several studies indicate that the use of carbonated solid wastes as SCMs is beneficial to the strength development of blended cement, especially the early-age strength for a 20–30% increase (Pan et al., 2015d, 2015).

3.2.3. Assessment of environmental and economic benefits

In terms of environmental impacts and benefits, the amount of heavy metals leached from alkaline solid wastes and the metrics of leaching of heavy metals from alkaline solid wastes are of great interest. Extensive studies have been carried out to evaluate the effect of accelerated carbonation, alkalinity (or pH) and mineral structure on the metal leaching behavior of wastes (Baciocchi et al., 2011; Salman et al., 2014; van Zomeren et al., 2011). Calcium-baring components in alkaline solid wastes are alkalinity contributors, thereby resulting in a high pH (>10). After carbonation with CO_2 gas, transformation of reactive CaO into calcium carbonate precipitates may decrease the pH of the solution to 6–9. In parallel with the decrease of pH, the leaching of heavy metals from wastes, such as Cu, Zn, Cr, Cd, V, Pb, Ba, and Sr, can be significantly restricted due to the formation of insoluble carbonates on the particle surface (Baciocchi et al., 2011; El-Naas et al., 2015).

Furthermore, oxidant states of heavy metals in solid wastes would lead to different leaching behaviours (Bacocchi et al., 2010).

The use of carbonated solid wastes as SCMs in blended cement mortar or concrete block can attain huge environmental and economic benefits (Pan et al., 2016c). It is noted that cement production is energy and material intensive: (1) it accounts for 4–5% annual global CO₂ emission (Gibbs et al., 2001), and (2) 1.5–1.7 tons of natural resources including 0.11–0.13 tons of coal are consumed per ton of cement clinker production (Kumar et al., 2006). Consequently, even with a 10% substitution ratio of carbonated product in cement mortar, a great amount of indirect environmental benefits can be revealed (Pan et al., 2016a). However, accelerated carbonation involves several energy-intensive processes, such as feedstock grinding, heating, pumps and pressurization. Energy consumption is responsible for the increase in additional CO₂ emission from processes, which might easily offset the credits from CO₂ fixation. Therefore, the environmental impact for different carbonation processes should be critically quantified via a life-cycle assessment (Xiao et al., 2014).

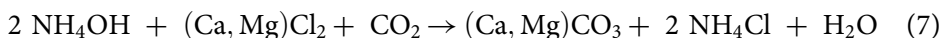
3.3. Indirect carbonation with production of high value-added chemicals

Indirect carbonation involves a few steps to proceed the carbonation process. It can be accomplished through a few different processes, such as indirect multistage gas–solid carbonation (Jo et al., 2014), pH swing method (Azdarpour et al., 2015), and ammonia extraction and caustic extraction (Mattila et al., 2012). Among these methods, the two-step pH swing process using regenerative ammonium salt and multi-stages indirect carbonation are considered as the most promising technologies to utilize industrial solid wastes under a mild condition. The followings briefly illustrate the principles and application of indirect carbonation as well as the product utilization as high value-added products.

3.3.1. Principles and applications (Process Design)

In the indirect carbonation, the extraction of calcium and/or magnesium ions from solid wastes is performed and followed by liquid and solid separation. CO₂ then dissolves into the liquid phase and precipitation of solid carbonates takes place in a separated step or different reactors. Several studies were carried out to evaluate the performance of indirect carbonation using different solid wastes such as steel slag (Mattila et al., 2012; Teir, 2008) and pulverized fuel ash (Velts et al., 2011). For the extraction step, a variety of solvents have been used: (1) acidic solvents such as acetic (Eloneva et al., 2010; Eloneva et al., 2008) and hydrochloric acid (Erlund et al., 2016), and (2) base or salt based solvents such as NaOH (Eloneva et al., 2008), ammonium chloride (Eloneva et al., 2011), ammonium bisulphate (Erlund et al., 2016), and aqueous ammonia (Hosseini et al., 2017). In the case of NH₄OH, the overall

carbonation reactions of leachate can be described as Eq. (7):



Regardless of their solution concentrations, the extraction efficiency of calcium ions using base or salt solvents follows the below sequence (Eq. (8)) (Jo et al., 2014):



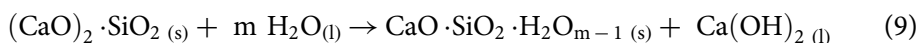
In the case of using 1.4 M ammonium bisulphate as the extractant, approximately 75–80% of magnesium content in serpentine can be extracted with the fraction 63–125 μm (Erlund et al., 2016). As the extraction proceeds, the deposition of an inert layer such as SiO_2 formed on the reactive surface, thereby preventing further dissolution of metal ions out from particles (Park and Fan, 2004).

3.3.2. Utilization of carbonate product as high value-added chemicals

Multi-stage indirect carbonation is an appropriate route for the production of high value-added chemicals, such as precipitated calcium carbonate and precipitated silica (Sanna et al., 2014). Compared to direct carbonation, the extraction of the metal ions in a separated step allows a better control in the morphology and particle size of products during the precipitation step. In indirect carbonation, a precipitated calcium carbonate with the purity of >99% can be attained, which is further proceeded to higher value added industrial materials including filters and coating pigments (Azdarpour et al., 2015; Pérez-Moreno et al., 2015; Said et al., 2013). The global demand for calcium carbonate is projected to reach 98.7 Mt on by 2020, driven by robust demands from paper and plastic end-user sectors (GIA, 2015).

3.3.3. Assessment of environmental and economic benefits

The dissolution of calcium silicate minerals (e.g., C_2S) during carbonation may break down the mineral structure (van Zomeren et al., 2011), as shown in Eq. (9). This would potentially release chloride and fluoride ions, as well as heavy metals such as V and Cr into liquid.



On the other hand, although the overall energy consumption of indirect carbonation is less than that of direct carbonation, the need of an energy-intensive process for regeneration of extractant might be a limiting factor from a full-scale application. The manufacturing of chemicals (such as solvents and extractants) for an extraction step would generate additional CO_2 emission. Therefore, a recovery process used chemicals with low energy consumption should be developed and implemented for indirect carbonation (Azdarpour et al., 2014; Xiao et al., 2014). According to the findings by Kodama et al. (2008), the energy consumption of the indirect

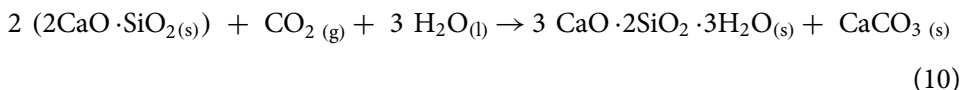
carbonation using NH_4Cl as the leaching agent was estimated as 300 kWh/ton- CO_2 . From another report by Hosseini et al. (2016), in the case of indirect carbonation for coal fly ash using NH_4Cl , the costs of CO_2 capture ranged from 135 to 1091 USD per tonne of CO_2 , corresponding to 61–333 USD per tonne of carbonate produced.

3.4. Carbonation curing for concrete block and cement mortar

Carbonation curing for concrete block and cement mortar can provide another alternative for CO_2 mineralization and valorization. Instead of using CO_2 in direct/indirect carbonation of alkaline solid wastes for the production of SCMs in cement preparation, CO_2 can be used in sequential curing processes, known as carbonation curing.

3.4.1. Principles and mechanisms

Carbonation curing of cementitious materials may improve their mechanical properties and durability. Normally, carbonation curing is being carried out by high-purity CO_2 gas ($\sim 99\%$) into a sealed chamber for curing concrete block or blended cement. This early-age carbonation in curing is the reaction between calcium silicates (or early hydration products) and CO_2 to produce a hybrid binder structure of calcium-silicate-hydrate (C-S-H, such as $\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$) matrix and CaCO_3 (El-Hassan and Shao, 2015), as described in Eq. (10).



To achieve a rapid carbonation rate, the relative humidity for carbonation curing should be maintained at 50–70% (Ashraf, 2016). For carbonation curing of OPC-based systems, rapid strength gains of the cementitious matrix, especially the early strength, could be observed since the presence of CO_2 accelerates the hydration of calcium silicates (Ashraf, 2016). During the carbonation process, the micron-sized CaCO_3 product is formed gradually in the C-S-H matrix, thereby building up a denser and more compacted structure (Mahoutian et al., 2014). This would be beneficial to the strength development of blended cement.

3.4.2. Carbonation curing models

Numerous models have been developed and validated to elucidate the behavior and mechanism of carbonation curing for concrete and/or cement-based materials. The most widely popular model to predict carbonation depth (X_c) in cement-based materials is shown in Eq. (11), based on Fick's first law (Housta and Wittmannb, 2002):

$$X_c(t) = \sqrt{2 \frac{D \times C_c}{C_r}} \times \sqrt{t} \quad (11)$$

where D is the effective diffusivity of CO_2 ; C_c is the CO_2 concentration in the curing atmosphere; C_r is the concentration of reactive compounds in materials; and

t is the carbonation exposure duration. Assuming the diffusion rate of CO_2 is constant, Eq. (11) can be simplified to Eq. (12):

$$X_c(t) = A \times \sqrt{t} \quad (12)$$

where A is an empirical constant. In reality, however, after a certain period of curing, carbonation depth does not reach a precise value as defined by a single number in Eq. (12) (Housta and Wittmannb, 2002). Moreover, the real CO_2 diffusivity should depend on multiple factors such as porosity of materials, relative humidity, CO_2 pressure and concentration (Ashraf, 2016), which is practically not a constant.

The carbonation resistance of concrete can be estimated by the Fib model (Eq. 13) (fib, 2006), in which the stochastic nature of concrete is induced during the curing with the experimental data.

$$X_c(t) = \sqrt{2 \times K_e \times K_c \times \left(K_t \times R_{ACC,o}^{-1} + \varepsilon_t \right) \times C_s \times W(t) \times \sqrt{t}} \quad (13)$$

where K_e is the environmental function considering the effect of humidity on CO_2 diffusivity; K_c is the execution transfer parameter considering the influence of curing on carbonation resistance; $R_{ACC,o}^{-1}$ [(mm^2/year)/(kg/m^3)] is the inverse effective carbonation resistance of material at a certain time; k_t is the regression parameter considering the effect of the test method on accelerated carbonation; and ε_t [(mm^2/year)/(kg/m^3)] is the error term considering inaccuracy due to carbonation methods.

3.4.3. Performance evaluation

Several studies have been performed to assess the effect of carbonation curing process on the properties of concrete (Ashraf, 2016), masonry (El-Hassan and Shao, 2015) and blended cement (Mo et al., 2015). The blended cement after carbonation curing exhibited higher strength and eligible soundness (Wu et al., 2009). In the course of carbonation curing, early hydration products can be converted to a crystalline microstructure, and subsequent hydration transformed amorphous carbonates into crystalline calcite (El-Hassan and Shao, 2015). Particularly, carbonation curing using highly pressurized CO_2 could result in faster strength development because of rapid penetration of CO_2 and carbonation of blended cement (Mo et al., 2015). Bukowski and Berger (1979) found that a compressive strength of 50 MPa for the nonhydraulic $\gamma\text{-C}_2\text{S}$ compact could be obtained after carbonation curing at 1 MPa for 15 min. Furthermore, in the case of OPC-based systems, carbonation reaction reduces the alkalinity of concrete, and hence makes the reinforcement susceptible to corrosion (Ashraf, 2016).

3.5. Summary

Alkaline wastes can be used to mineralize great amount of CO_2 via accelerated carbonation, while manufacturing green materials and/or high value-added products

such as glass ceramics and precipitate calcium carbonate. Both the environmental and economic benefits can be realized, especially if the wastes are generated nearby the source of CO₂. To achieve a cost-effective manner, appropriate carbonation efficiency (e.g., a carbonation conversion >85%) should be designated. In addition, mineralization of CO₂ using alkaline solid wastes could be linked to utilize wastewater for large-scale application. At present, significant technological breakthroughs in reactor design, waste-to-resource supply chain, and system optimization should be needed before deployment can be considered.

4. Catalytic reduction of CO₂ to organic fuel for transport

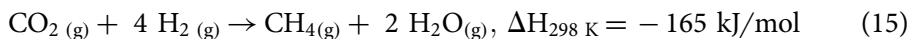
Converting CO₂ into organic transport fuels is an important CO₂ valorization option since the transport sector is a large contributor to GHG emissions. However, reducing CO₂ requires high energy substances or electro-reductive processes due to the chemically inert property of CO₂. In fact, the amount of energy required for reforming CO₂ into organic fuels may exceed the amount of energy that can be recovered (Schakel et al., 2016). Therefore, it only can become a viable option at the place where excess energy (e.g., intermittent renewable energy) is available. In this section, the concept of sustainable organic fuel for transport (SOFT) is first illustrated and then reviewed with the details of state-of-the-art technology information.

4.1. The concept of SOFT

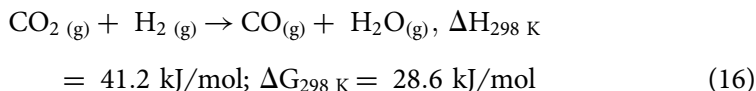
Since hydrocarbon fuels are used for the majority of transportation as energy sources, a concept of SOFT was developed to provide compatible affordable mobility using carbon-neutral liquid fuels. Figure 5 shows the concept of sustainable organic fuel for transport (SOFT) incorporated with renewable energy storage and CO₂ capture and valorization. This concept retains the use of low-cost internal combustion engines and liquid fuel systems (Pearson et al., 2012). Using heat, electricity and light from renewable energy, CO₂ and H₂O can be converted to various hydrocarbon fuels in a nonbiological (chemically catalytic) process. SOFT can be produced by the following three steps: (1) CO₂ capture from either flue gas or ambient air, (2) storage of the renewable energy as chemical energy by dissociation of CO₂ and/or H₂O, and (3) synthesis of fuels using the dissociation products (Graves et al., 2011). In other words, three key components are required for producing SOFT: (1) H₂ source, (2) CO₂ source, and (3) catalysts.

Integration of electrochemical water-splitting (Eq. (14)) with renewable energy can serve to lower GHG emissions, while buffering the intermittency and fluctuations of renewable energy (Cho and Hoffmann, 2017; Olah et al., 2009). Theoretically, the power consumption of water electrolysis is 39.4 kWh per kg of hydrogen produced (Simbeck and Chang, 2002). In practice, considering the power needed for a complete electrolysis, the conversion efficiency of water to hydrogen is in a range between 73% and 85% depending on systems (IEA, 2004; Ivy, 2004). In other

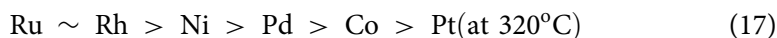
a catalytic reaction as shown in Eq. (15), also known as Sabatier reaction.



The Sabatier reaction is accompanied by a side reaction, so-called the reverse water-gas-shift reaction as shown in Eq. (16). Since this side reaction will reduce the yield of methane, a proper process control should be developed to avoid it.



The commonly used catalysts for methanation process are based on Group VIII metals, such as Ni and Ru, and supported on various porous materials (Nizio et al., 2016). The catalytic activity of transitional metals in CO₂ methanation is in the following order (Duyar et al., 2016):



For CO₂ methanation, if three components (i.e., Ni, La₂O₃, and Ru) are combined at a proper ratio, the prominent synergy that is far from the sum of the activity of each catalyst can be obtained (Inui and Takeguchi, 1991). A significant CO₂ conversion was also observed when the reaction temperature was set above 180°C (Mihet and Lazar, 2016). Although Ni-based catalysts are commonly used for CO₂ methanation, they will be oxidized and deactivated by flue gas containing significant amounts of air. Therefore, Ru remains the favorite catalyst due to its low price and excellent performance even at low temperature.

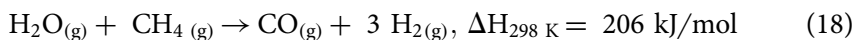
Recently, Duyar et al. (2016) developed a process to simultaneously capture and convert CO₂ as an endothermic CO₂ desorption step of a traditional adsorbent is coupled with the exothermic hydrogenation of CO₂ over a catalyst occurs to produce methane. This process proceeds in a single reactor operating at 320°C and of an ambient pressure to capture CO₂ from flue gas and then produce methane upon exposure to renewable hydrogen. A dual function catalyst containing Rh and dispersed CaO (>1% Rh 10% CaO/γ-Al₂O₃) was developed to convert CO₂ to methane.

4.2.2. Dry reform of methane to syngas

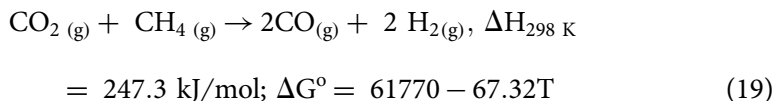
Syngas is a gas mixture consisting primarily of CO and H₂, with a small amount of CO₂. It can be produced from methane via a variety of reforming techniques, such as steam reforming (Esteban-Díez et al., 2016; Koo et al., 2016), dry reforming (Ahmed et al., 2017; Pakhare and Spivey, 2014), partial oxidation (Duan et al., 2017), autothermal reforming (Mota et al., 2016), and chemical looping reforming (Huang et al., 2016; Neal et al., 2015). Partial oxidation reaction is applied at a temperature lower than 600°C (Lau et al., 2011), while dry and/or steam reforming

reactions are more commonly adapted at a temperature higher than 600°C (Yang et al., 2014). In industrial practices, these three methane reforming processes are operated simultaneously in a single reactor, named the tri-reforming system.

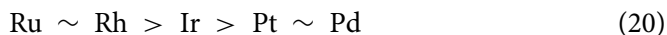
The syngas can be used in chemical energy transmission, upgraded to higher alcohols through fermentation, or utilized in the Fischer-Tropsch synthesis to produce a wide range of chemicals such as higher alkanes and oxygenates. Steam reforming of methane is a commercial method of producing syngas (or hydrogen). As shown in Eq. (18), steam reacts with CH₄ to produce syngas at high temperatures of 700–1100°C and in the presence of a metal-based catalyst such as Ni.



Due to climate change, water resource is sometimes limited in some regions to be used for producing syngas via the steam reforming reaction. Under this circumstance, dry reforming of methane to syngas using CO₂ can be deployed; (Eq. (19)). Conversion of these two compounds to higher value fuels or chemicals might be profitable. This highly endothermic reaction requires operating temperatures of 800–1000°C to minimize the thermodynamic driving force for carbon deposition (Pakhare and Spivey, 2014). Compared to steam (H₂O) reforming of CH₄ (Eq. 18), the CO₂-based reforming process produces syngas with lower H₂/CO ratios.



The most widely used catalysts for the CH₄ dry reforming process are Ni-based; however, they typically undergo severe deactivation due to carbon deposition (Pakhare and Spivey, 2014). Thus, researches should focus on a thermally stable catalyst that can resist the deactivation caused by carbon deposition and sintering. The resistance of catalyst to deactivation can be promoted by choosing an appropriate basic support and a promoter as well as by using noble metals with high activity and of great carbon deposition resistance. Recently, noble metals have been studied to be incorporated with the Ni catalyst. In general, the activities of noble metals supported catalysts in the CH₄ dry reforming are in the following order (Jones et al., 2008; Rezaei et al., 2006).

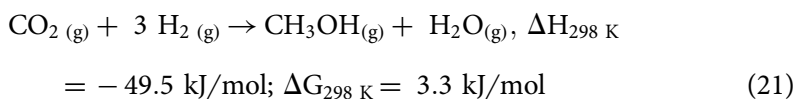


The activity of a catalyst depends on the type of the metal and support, the interaction between the metal and support, particle size of the metals, and surface area of the support. For instance, the support with Lewis basic sites, such as Al₂O₃, MgO, and CaO, can promote the ability of deactivation resistance while enhancing the adsorption capacity of CO₂ (Ma et al., 2009). For all the catalysts, the CO₂

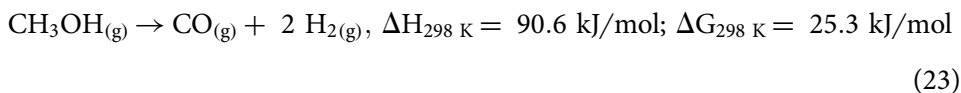
conversion is generally higher than the CH₄ conversion due to the reverse water-gas-shift reaction.

4.2.3. CO₂ hydrogenation to methanol

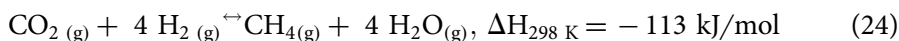
Catalytic reduction of CO₂ to methanol (CH₃OH) generally starts from hydrogenation using a suitable catalyst at a temperature of 413 K and a pressure of 1 MPa (Ma et al., 2009), as shown in Eq. (21). This reaction is an exothermic reaction. Therefore, a decrease in temperature or an increase in reaction pressure should be favored for the reaction from a thermodynamic point of view (the Le Chatelier's principle). Considering the reaction kinetics, the reaction temperature should be maintained of 513 K to facilitate CO₂ activation and the subsequent methanol formation (Ma et al., 2009).



Along the way, several side reactions including the reverse water-gas-shift reaction (Eq. (18)) and secondary reaction (Eq. (23)) occur, producing CO as an intermediate precursor:



The reverse water-gas-shift reaction consumes extra H₂ and results in a reduction of CH₃OH production and an increase of water production, which is detrimental to the active sites of catalysts (Alaba et al., 2017). On the other hand, at a low pressure, at a high temperature and a H₂/CO₂ ratio greater than 3 (Szailer et al., 2007), CO₂ reforming occurs with supported noble metal catalysts such as Rh, Ru, Ir, Pd, and Pt via Eq. (24). The chemisorption of CO₂ on supported noble catalysts (such as Rh, Ru, and Pd) in hydrogenation can initiate the formation of metal hydride complexes on the surface of the catalysts (Olah and Molnár, 2003).

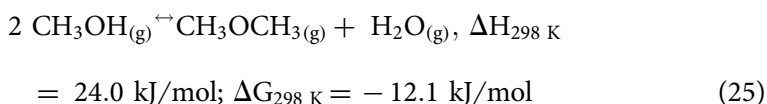


Therefore, it is challenging to rationally design a stable catalyst with a high CH₃OH selectivity to circumvent the formation of undesired by-products. The CO₂ conversion and CH₃OH selectivity could be determined by thermodynamic equilibrium efficiencies, particularly to the formulation of a catalyst. Aside from being used as a transport fuel, CH₃OH is a common feedstock and/or a building block in chemical processes to produce versatile important chemicals such as chloromethane, acetic acid, methyl tert-butyl ether, alkyl halides, formaldehyde, and dimethyl carbonates (DMC). In addition, methanol can be used to produce

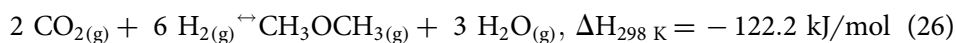
(1) higher hydrocarbons through a methanol-to-gasoline route, and (2) unsaturated hydrocarbons through methanol-to-olefins or methanol-to-propene routes (Aresta et al., 2016).

4.2.4. CO₂ hydrogenation to DME

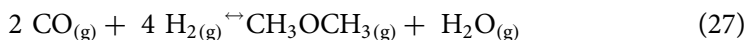
DME can be synthesized mainly in ways in two approaches. One is a two-step method, i.e., methanol synthesis on metallic sites followed by dehydration on solid acid catalysts. In the presence of a solid acid catalyst, methanol formed as Eq. (21) could be dehydrated to form DME as Eq. (25). Solid acid catalysts, which can dehydrate methanol to DME, include γ -Al₂O₃, silica-alumina and different types of zeolites (e.g., HZSM-5) (Marcos et al., 2016), as well as pillared clays (PILC) (Śliwa et al., 2014). In addition, both Al- and Nb-based catalysts have exhibited high catalytic activity and selectivity because they have strong Lewis and Brønsted acid sites (da Silva et al., 2016). Nb–O bonds are mainly associated to Brønsted acid sites during catalytic reaction.



The other way to synthesize DME is a single-step method or direct CO₂ hydrogenation, (Eq. (26)). This reaction comprises a bi-functional catalyst constituted by metallic acid sites.



Similarly, as shown in Eq. (27), DME can be formed via one-step synthesis from syngas or bio-syngas (Haro et al., 2013). The efficiency of syngas conversion to methanol (Eq. (21)) or DME (Eq. (25)) strongly depends on the ratio H₂/CO present in the syngas. Syngas with a H₂/CO ratio close to one is suitable for direct synthesis of DME (Schakel et al., 2016).



The feasibility of the single-step synthesis from a mixture of CO₂ and H₂ can ensure a lower thermodynamic limitation in respect of the conventional two-step approach. From a thermodynamic point of view, low temperatures or high pressures should be favored for the synthesis of DME via the direct CO₂ hydrogenation reaction. From a kinetic point of view, however, only increasing reaction temperature above 240°C could facilitate the CO₂ activation rate (Bonura et al., 2016). In direct synthesis of DME, a wide range of feed gas compositions and operating conditions can be used (Erdener et al., 2011). Regarding the catalysts, the direct catalytic hydrogenation of CO₂ into DME is typically performed in the presence of

physical/mechanical mixtures of a Cu-based methanol synthesis catalyst and a solid acid catalyst (Bonura et al., 2016).

4.3. Catalyst performance and design criteria

Table 3 presents the important factors determining the residence time of reactants in the reactor and consequent catalytic activity. Reaction temperature and pressure have a significant influence on reactions in gas phase. The effect of temperature and pressure on CO₂ conversion and CH₃OH selectivity has been evaluated (Gaikwad et al., 2016). In addition, gas hourly space velocity (GHSV) plays an important role in the catalytic reduction of CO₂. It is reported that a low GHSV requires longer time between catalyst surface and reacting gas. Regarding the formula and preparation of catalyst, the interaction between the metal and support plays an important role in the catalyst performance. On the other hand, the uses of promoters can enhance the structure and electronic properties of the catalysts, thereby improving CO₂ conversion and product selectivity.

Table 4 presents the performance of CO₂ catalytic reactions and their product formation over different types of catalysts. To convert CO₂ into organic fuels through a catalytic reaction, transitional metals have been utilized as catalysts on metal oxide supports (e.g., Al₂O₃). The CO₂ molecule exhibits a wide range of coordination and reaction modes in its homo- and polynuclear metal hydride complexes (Ravanchi and Sahebdehfar, 2003). For example, Ni-based catalysts are widely applied for CO₂ methanation due to their good compromise between high activity and low cost (Duan et al., 2011). Ni-based catalysts are not easily poisoned by CO either, compared to the expensive Pt-based catalyst. For CO₂ methanation, both Ru and Rh also can be used as a catalyst with sufficient activity (Duyar et al., 2016). Furthermore, dual function materials containing a CO₂ adsorbent and a methanation catalyst could be effective in adsorbing and converting CO₂ in the flue gas.

Table 3. Important factors determining residence time of reactants in reactor and consequent catalytic activity.

Category	Factors	Effects
Operation	H ₂ /CO ₂ ratio	Related to CO ₂ conversion, and product selectivity. This ratio should be maintained at 3 (Bansode and Urakawa, 2014).
	Pressure	Related to concentration of reactants, and collision speed of particles.
	Temperature	Related to product selectivity, and collision speed of particles
Catalyst	GHSV	Related to residence time of the reactants in reactor.
	Metal	Affect the activity of catalyst to CO ₂ conversion.
	Support	Affect the active site dispersion, and stability.
	Promoter	Affect the dispersion of metal oxide catalysts. Common promoters include Cr ₂ O ₃ , ZrO ₂ , Al ₂ O ₃ , CaO, K ₂ O, CeO ₂ , and Ga ₂ O ₃ .

Table 4. Performance of CO₂ catalytic reaction and its product formation over catalysts.

Category	Catalyst	Catalyst preparation ^a	Feed gas composition	Press. (MPa)	Temp. (K)	Conversion (%)	Reaction kinetics ($\mu\text{mol}/\text{min}/\text{g}_{\text{cat}}^{\text{c}}$)	Selectivity (%) or yield (%) ^d					Reference
								MeOH	EtOH	DME	CH ₄	CO	
Methanation to methane	Ni/CeO ₂	ETD	CO ₂ /H ₂ /He (1:4:5)	—	573	CO ₂ : 80	—	—	—	—	Y: 92	Y: 8	(Fukuhara et al., 2017)
	Ni/CeZrO _x	WI	CO ₂ /H ₂ (1:4)	—	723	CO ₂ : 85 ^b	—	—	—	—	—	—	(Nizio et al., 2016)
	5Ni/Ce60Zr40O _x	SG	CO ₂ /H ₂ (1:4)	0.1	423–673	CO ₂ : 79.7 H ₂ : 76.1	CO ₂ : 7.2–113.9 × 10 ⁶	—	—	Y: 99.3	Y: 0.6	—	(Ocampo et al., 2011)
Dry reform to syngas	Ni-Pt/Al ₂ O ₃	WI	CO ₂ /H ₂ (1:4)	0.1	573	CO ₂ : 83.4	TOF: 3.9 × 10 ⁻² s ⁻¹	—	—	S: 97	—	—	(Mihet and Lazar, 2016)
	Ni-Pd/Al ₂ O ₃	WI	CO ₂ /H ₂ (1:4)	0.1	573	CO ₂ : 90.6	TOF: 3.7 × 10 ⁻² s ⁻¹	—	—	S: 97	—	—	(Lazar, 2016)
	20Pt/ZrO ₂	IWI	CO ₂ /CH ₄ /He (1:1:18)	0.003	823	CO ₂ : 36.8 CH ₄ : 28.9	CO: 1.3 × 10 ⁴	—	—	—	—	—	(Souza et al., 2001)
	Co/La-ZrO ₂	CPM	CO ₂ /CH ₄ /Ar (1:1:2)	—	619	CO ₂ : 31.2 CH ₄ : 20.3	—	—	—	—	—	S: 99.4 Y: 20.1	(Yabe et al., 2017)
	Ni/La-ZrO ₂	CPM	CO ₂ /CH ₄ /Ar (1:1:2)	—	555	CO ₂ : 24.8 CH ₄ : 22.8	—	—	—	—	—	S: 100 Y: 22.8	(Yabe et al., 2017)
	1Pd(Cl)-1Ni/Y ₂ O ₃	WI	CH ₄ /CO ₂ /O ₂ (5:4:1)	0.1	973	CO ₂ : ~72 CH ₄ : ~70	—	—	—	—	—	—	—
CO ₂ hydrogenation to methanol	0.86Pd-CeO ₂	WI	CO ₂ /CH ₄ /He (1:1:12)	0.1	1073	CO ₂ : ~98 CH ₄ : ~94	—	—	—	—	—	H ₂ /CO: 0.8	(Singha et al., 2017)
	Cu/MgO	CP	CO ₂ /H ₂	3	523	—	MeOH: 47.1	—	—	—	—	—	(Kunkes et al., 2015)
	CuZnMg/ γ -Al ₂ O ₃	WI	CO ₂ /H ₂ (1:3)	2	523	CO ₂ : 12.1	MeOH: 16.1	—	—	S: 2.4	S: 61.6	—	(Ren et al., 2015)
	Cu/ZnO/Al ₂ O ₃	CP	CO ₂ /H ₂ (1:3)	5	543	CO ₂ : 2	—	—	—	—	—	—	(da Silva et al., 2016)
	Cu/ZnO/Al ₂ O ₃	CP	CO ₂ /H ₂	3	523	—	—	—	—	—	—	—	(Kunkes et al., 2015)
Cu/ZnO/Al ₂ O ₃	CP	CO ₂ /H ₂	44.2	553	CO ₂ : 88.5	MeOH: 468.8	—	—	—	—	—	(Gaikwad et al., 2016)	

Cu-ZnO-Al ₂ O ₃	CP	CO ₂ /H ₂ (1:3)	4.1	523	CO ₂ : 18.4	MeOH: 28.8 CO: 75.6	S: 27.0	—	—	S: 73.0	(Jiang et al., 2015)
Pd-Cu/SiO ₂	CP	CO ₂ /H ₂ (1:3)	4.1	523	CO ₂ : 6.6	MeOH: 18.6 CO: 36.6	S: 34.0	—	—	S: 66.0	(Jiang et al., 2015)
5Pd/ZnO	SI	CO ₂ /H ₂ (1:3)	2	523	CO ₂ : 10.7	—	S: 60.0	—	—	S: 39.0	(Bahruij et al., 2016)
5Pd/ZnO	IWI	CO ₂ /H ₂ (1:3)	2	523	CO ₂ : 8.7	—	S: 2.2	—	—	S: 97.8	(Bahruij et al., 2016)
Fe/Mo ₂ C (carbides)	IWI	CO ₂ /H ₂ (1:3)	4	408	CO ₂ : 1.0	CO ₂ : 2.8	S: 87.0	S: 0	S: 7.2	S: 4.1	(Chen et al., 2016)
Fe/Mo ₂ C (carbides)	IWI	CO ₂ /H ₂ (1:3)	4	473	CO ₂ : 10	CO ₂ : 70.1 TOF: 3.8 × 10 ⁵	S: 58.0	S: 16.0	S: 8.1	S: 6.8	(Chen et al., 2016)
Pd/Mo ₂ C (carbides)	WI	CO ₂ /H ₂ (1:3)	4	408	CO ₂ : 1.0	CO ₂ : 4.9	S: 95.0	S: 0	S: 1.6	S: 3.6	(Chen et al., 2016)
Pd/Mo ₂ C (carbides)	WI	CO ₂ /H ₂ (1:3)	4	473	CO ₂ : 10	CO ₂ : 80.3	S: 68.0	S: 11.0	S: 7.6	S: 9.6	(Chen et al., 2016)
Cu/ZnO/Al ₂ O ₃	WI	CO ₂ /H ₂ (1:3)	5	543	CO ₂ : 9	—	S: 69	—	S: 31	—	(da Silva et al., 2016)
Cu/ZnO/Nb ₂ O ₅	WI	CO ₂ /H ₂ (1:3)	5	543	CO ₂ : 2	—	S: 95	—	S: 5	—	(da Silva et al., 2016)
Cu/Zn/Zr-FER (zeolite)	CP	CO ₂ /H ₂ /N ₂ (3:9:1)	5	553	CO ₂ : 30	DME: 270	—	—	S: 62.0	—	(Bonura et al., 2016)
Cu/Zn/Al slurry	Liquid	CO/H ₂ (1:1)	4	553	CO: 15.8	DME: 3.83	S: 1.8	—	S: 57.1	—	(Gao et al., 2009b)
CuCe/PILC	WI	CO ₂ /H ₂ (1:3)	4	523	CO ₂ : ~5	—	S: 40	—	S: 46	S: 13	(Marcos et al., 2016)
CuCe/PILC	WI	CO ₂ /H ₂ (1:3)	4	573	CO ₂ : ~12	—	S: 19	—	S: 31	S: 50	(Marcos et al., 2016)
9Nb/TiO ₂	IWI	CH ₃ OH	0.006	573	11.3	CH ₃ OH: 232	—	—	S: 93	S: 7	(Ladera et al., 2012)

^aEED: evaporation to dryness; SG: sol-gel method; CP: coprecipitation; SI: sol-immobilization; WI: wet impregnation; IWI: incipient wetness impregnation; CPM: complex polymerized method.

^bCatalytic reaction was applied with a plasma.

^cTOF: turnover frequency at 150 °C, defined as moles of methane formed per active metal particle per unit time, taking into account the total metal dispersion as determined from the H₂ chemisorption tests.

^dS: selectivity (%); Y: yield (%).

In CO₂ hydrogenation, the most prominent metals are Zn, Cu, Co, Ni, Rh, Pt, and Pd due to their relatively high hydrogenation activity. The aforementioned metals also can be rationally incorporated into different modifiers (promoters) such as Al, Zr, Ti, Si, Ga, Cr, B, V, and Ce oxides (Marcos et al., 2016). For example, in the case of the conventional catalyst (Cu/ZnO/Al₂O₃), metallic copper is the active catalyst and ZnO is used to increase the Cu dispersion on the support. Gao et al. (2009b) found that CuO and Cu⁺ species played an essential role in the synthesis of methanol. However, the Cu-based catalysts usually cause undesired CO formation via the reverse water-gas-shift reaction (Kunkes et al., 2015).

In the case of methanol dehydration to DME, solid acid catalysts should be introduced. Cu-, Al-, and Nb-based catalysts exhibited high selectivity to DME because they provide strong Lewis and Brønsted acid sites. Usually, these catalysts are incorporated with other metallic elements. Marcos et al. (2016) observed in their study that the CuCe/PILC catalyst exhibited the highest intensity of Lewis band, in comparison to the other catalysts such as Cu/PILC and CuNb/PILC. On the other hand, CO₂ hydrogenation is initiated by the CO₂ activation to form intermediates on basic sites (i.e., HCOOH*) that are subsequently hydrogenated on the metallic sites producing methanol (Ren et al., 2015). As a result, balancing the number of metallic, basic and acid sites on catalysts is imperative to DME production. Furthermore, as the temperature increases, the DME selectivity decreases while the methane selectivity increases (Marcos et al., 2016).

The economic feasibility of methanol production from CO₂ depends on (1) the price of H₂ and CO₂, (2) the quality of H₂ and CO₂ (a purity of 99% will be desirable), (3) the price of the catalyst, and (4) the plant investment and the operation and maintenance. In CO₂ catalytic hydrogenation, a highly stable and active catalyst should be developed to enhance CO₂ conversion efficiency for economical production. In addition to the types of catalyst materials, the synthesis method, reactor design and an economically viable renewable energy source are all important factors (Alaba et al., 2017). Similarly, in photocatalytic systems, metal-organic complex materials and semiconducting such as TiO₂ and CdS are commonly employed. Despite their potential environmental benefits, a long-lasting challenge in the photocatalytic reactions is low efficiency of CO₂ reduction caused by (1) fast electron-hole (e⁻-h⁺) recombination rates, (2) low CO₂ affinity of the photocatalyst, and (3) complicated backward reactions (Wang et al., 2014). On the other hand, in an electrocatalytic system, Cu, Ag and Sn are often applied as a catalyst to convert CO₂ into various hydrocarbon products. However, they typically suffer from low electrochemical performance in terms of activity and selectivity (Wu and Zhou, 2016).

4.4. Summary

CO₂ valorization can be integrated with a renewable energy storage system to produce organic transport fuels such as methane, syngas, methanol, and dimethyl

ether. To move forward successful commercialization, both a high-quality H₂ source and a cost-effective catalyst are the essential components. In fact, H₂ can be generated via electrolysis of water, served as a storage media of intermittent renewable energy. After that, CO₂ molecules can combine with H₂ (or proton) on catalyst sites to form various transport fuels and chemicals. It is noted that reaction temperature and pressure play a significant role on CO₂ catalytic reactions. The future research should focus on developing a thermally stable catalyst with great resistance and activity to intensify CO₂ conversion for economical production. For instance, the development of dual function materials for simultaneously adsorbing and converting CO₂ in the flue gas could be beneficial.

5. Transformation of CO₂ to value-added chemicals

To date, the vast majority of carbon resources still are on fossil-based type such as crude oil, natural gas and coal (Liu et al., 2015). For sustainability, we need to reduce our rely on the fossil-based carbon resources. In addition to biomass, CO₂ offers a great possibility to create a sustainable “carbon economy system.” Although more than 20 catalytic processes for CO₂ reductive conversion have been developed over the past two decades, industrially viable processes still are scarce. In fact, only the reaction of CO₂ with highly reactive (energy-rich) substrates such as epoxides and aziridines can be economically feasible. The carbon-neutral products from these affordable processes include polycarbonates, polycarbamates, cyclic carbonates (such as dimethyl carbonates) and carbamates. In this section, we review the advances on green synthetic processes using CO₂ as a building block for the production of different organic chemicals, especially urea, carbamates, dimethyl carbonates, and formaldehyde.

5.1. Building block for organic intermediates

Valorization of CO₂ for the synthesis of organic chemicals has been extensively explored (Altenbuchner et al., 2014). Numerous chemicals such as methane, ethanol and polymers can be produced from CO₂ reduction reaction using catalyst (Chiang and Pan, 2017f). As shown in Figure 6, CO₂ is an abundant C1 building block which can be incorporated to synthesize carbonyl, carboxylic acid, carbonate and carbamate functional groups. The same concept for SOFT synthesis is also applied that a decrease in the CO₂ emission can be achieved only by using hydrogen from nonfossil resources, such as electrolysis of water via renewable energy (e.g., solar and wind).

According to the oxidation state of carbon atom, the CO₂ conversions can be classified into two main categories:

- (1) **CO₂-modified type reaction:** the oxidation state of carbon remains the same (i.e., +4) before and after the reaction. This reaction which is typically carboxylation does not require substantial amount of external energy (Alper and Yuksel Orhan, 2016). The products of this reaction include ureas

Table 5. Market potentials and amount of CO₂ use for production of high value-added chemicals.^a

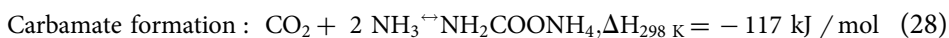
Category	Chemicals	Molecular formula (Linear or Hill Notation)	C _{oxi_state}	Market (Mt/y)	CO ₂ use (Mt/y)	Market price at Jan. 2017 ^b
Organic Fuels	Methane	CH ₄	-4	—	—	—
	Methanol	CH ₃ OH	-2	60–100	2–10	0.4 USD/kg
Organic chemicals	DME	CH ₃ OCH ₃	-2	6.5–14.7	12.4–28.1	1–5 USD/kg
	Formaldehyde	CH ₂ O	0	9–21	13.1–30.5	92.2 USD/L (37 wt.% purity)
	DMC	(CH ₃) ₂ CO	+1	10	4.9	60.7 USD/L (99% purity)
	Acrylate	CH ₂ =CHCOOH	+3	5	1.5	483 USD/L (99% purity)
	Salicylic acid	2-(HO)C ₆ H ₄ CO ₂ H	+3	0.07	0.03	179.4 USD/kg (>99% purity)
	Methyl carbamate	NH ₂ COOCH ₃	+4	—	—	135.4 USD/kg (98% purity)
	Urea	(H ₂ N) ₂ CO	+4	150–180	112–132	109.5 USD/kg (>98% purity)
	Formic acid	HCOOH	+2	0.7–1.0	0.9	60.0 USD/kg (>95% purity)
	Ethylene carbonate	C ₃ H ₄ O ₃	+4	0.08	0.04	44.8 USD/kg (98% purity)
	Carbamates	RNH–COOR	+4	>6	1	—
	Polycarbonates	–[OC(O)OCH ₂ CHR] _n –	+4	5	1	—
	Linear carbonates	OC(OR) ₂	+4	>2	0.5	—
	Magnesium carbonates	MgCO ₃	+4	27.7	7.2	302.5 USD/kg (>99% purity)
Inorganics	Calcium carbonates	CaCO ₃	+4	829	365	236.0 USD/kg (>99% purity)
	Potassium carbonates	K ₂ CO ₃	+4	—	—	164.0 USD/kg (>99% purity)
	Sodium carbonates	Na ₂ CO ₃	+4	13.7	5.7	153.0 USD/kg (>99% purity)

^aAvailable data was gather from the literature (Aresta, 2010a; Aresta et al., 2013; Aresta et al., 2017; Aresta et al., 2016; Bolen, 2016; Group, 2007; Lee Bray, 2016).

^bmarket price at 2017/01 for a reagent-class grade.

synthesized and applied in a wide variety of fields, such as pharmaceuticals, petrochemicals, and agrochemicals. Currently, more than 90% of worldwide production of urea is used as a nitrogen-release fertilizer.

After development of the ammonia (NH_3) synthesis via the Haber-Bosch method, technologies to produce urea from NH_3 and CO_2 have advanced rapidly. Since 2001, urea is produced on an industrial scale exclusively based on this method (Meessen, 2005). It consists of two sequential equilibrium reactions at elevated temperatures and pressures, so-called the Basaroff reaction, as shown in Eqs. (28) and (29). The first reaction is fast and exothermic (Eq. 28), where CO_2 and liquid NH_3 are converted to ammonium carbamate ($\text{NH}_2\text{COONH}_4$). The second step, which is slow and endothermic, is related to dehydration of ammonium carbamate to produce urea and water at high temperatures and pressures. Since the urea conversion step is a reversible reaction, a variety of dehydrating agents should be applied as a condensating reagent to prevent the reverse reaction from occurring.



In fact, urea can be produced at a mild temperature and pressure; the conversion efficiency is low though (Quaranta and Aresta, 2010). The CO_2 conversion efficiency, usually ranged between 50% and 80%, increases as temperature and NH_3/CO_2 ratio increase, as well as decreases with increasing $\text{H}_2\text{O}/\text{CO}_2$ ratio (Maxwell, 2004). According to the Le Chatelier's principle, a typical compromise conditions are at a high temperature around 463 K for the first step, and under high pressure of 14.0–17.5 MPa for the second step. However, there are still several side reactions which may result in decomposition of urea, e.g. (1) hydrolysis of urea, (2) formation of biuret ($\text{NH}_2\text{CONHCONH}_2$) from urea, and (3) formation of isocyanic acid (HNCO) from urea. From an economic point of view, different modifications on the urea synthesis technologies have been proposed to maximize the product yield and energy efficiency. Theoretically, controlling the amount of CO_2 , H_2 , and N_2 in the system would demonstrate an effective mass production of urea (Eq. (30)) (Yahya et al., 2017b):

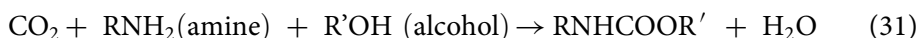


Recently, a nanowires-based hybrid nanocatalyst system with a concept of magnetic induction has been proposed and developed at ambient reaction conditions (Yahya et al., 2017b). Yahya et al. (2017a) suggest that the yield enhancement might be attributed to the increases in the singlet to triplet conversion. In their study, $\alpha\text{-Fe}_2\text{O}_3$ was used as a nanocatalyst to achieve the highest urea yield of $\sim 11,240$ ppm at oscillating magnetic field frequency of 0.5 GHz (Yahya et al., 2017a).

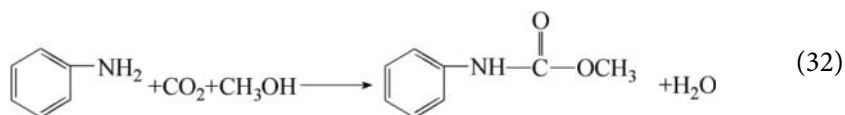
5.3. Synthesis of carbamates from amine and alcohol

Carbamates (RNH—COOR) are being used for production of pesticides, germicides, pharmaceuticals, and other organic chemicals. Important carbamate compounds include aromatic carbamates such as methyl N-phenyl carbamate (MPC), as well as alkyl carbamates such as methyl carbamate (MC), ethyl carbamate (EC), and butyl carbamate (BC). From the green chemistry point of view, CO₂ can be used to generate the carbamates from amines and alcohols, which is considered as an environmentally benign route. At an ambient temperature and pressure, CO₂ can easily combine with amines to form the corresponding carbamic acids. If alcohols are used as the alkyl source, however, the subsequent dehydrative condensation to carbamates proceeds slowly (Ion et al., 2008). Thus, an excess amount of a dehydrant is often used to overcome the equilibrium limitation.

Few studies were reported on direct synthesis of carbamates from CO₂, amines and alcohols. As shown in Eq. (31), it is an attractive process for the synthesis of carbamates since it is a phosgene- and halogen-free process. The reaction still typically suffers from both thermodynamic and kinetic limitations. As a result, a suitable catalyst should be used to overcome the kinetic impediments. In particular, the catalyst should be designed with a water-tolerance to avoid deactivation by cogenerated H₂O since water is formed as the only reaction byproduct.



For instance, the MPC can be synthesized from aniline, CO₂ and methanol via Eq. (32). A variety of solid catalysts, such as Cu-Fe/ZrO₂-SiO₂ (An et al., 2014), Zn(OAc)₂ (Li et al., 2014a) and Pb-related components (Gao et al., 2009a), have been developed and applied for MPC synthesis from CO₂.



On the other hand, the alkyl carbamates (e.g., MC, EC, and BC) are a class of important intermediates, which are widely used as an alternative carbonyl source in many carbonylation reactions (Li et al., 2011). Carbamate groups can be incorporated in numerous methods to synthesize carbamate esters (Quaranta and Aresta, 2010); this include the transfer of carbamate group to (1) alcohols, (2) alkyl halides, (3) acylating agents, (4) epoxides, (5) C—C double bonds, and (6) C—C triple bonds. Syntheses of N-alkyl carbamates from amines, CO₂, and alcohols (or alkyl halides) have been extensively studied. Recently, Li et al. (2011) developed a direct catalytic synthesis for MC, EC, and BC from NH₃, CO₂, and alcohols with

Table 6. Catalytic CO₂ reactions for synthesis of carbamates.

Catalysts ^a	Alcohol (alkyl)	Amine ^b	Products	Conditions	Conversion (%)	Yield (%) ^b	Selectivity (%) ^b	Reference
Cu-Fe/ZrO ₂ -SiO ₂	MeOH	Aniline	MPC	P = 1 MPa; T = 433 K; t = 7 hr; w/ acetonitrile (as solvent)	MeOH: 11.7; Aniline: 11.1	MPC: 1.2; DPU: 2.5	MPC: 11.1; DPU: 22.8	(An et al., 2014)
Cu-Fe/ZrO ₂ -SiO ₂	MeOH	Aniline	MPC	P = 1 MPa; T = 433 K; t = 7 hr; w/ methanol (as solvent)	MeOH: 16.8; Aniline: 2.9	MPC: 1.4; DMC: 3.5	MPC: 49.3; DPU: 4.1	(An et al., 2014)
Zn(OAc) ₂ /SiO ₂	DMC	Aniline	MPC	T = 443 K; t = 7 hr	Aniline: 98.1	MPC: 93.8	MPC: 93.5; NMA: 4.9	(Li et al., 2014a)
PbO	DMC	DPU	MPC	P = 1 MPa; T = 433 K; t = 4 hr	DPU: 99.7	MPC: 96.6	—	(Gao et al., 2009a)
PbCO ₃	DMC	DPU	MPC	P = 1 MPa; T = 433 K; t = 4 hr	DPU: 99.5	MPC: 96.1	—	(Gao et al., 2009a)
2PbCO ₃ -Pb(OH) ₂	DMC	DPU	MPC	P = 1 MPa; T = 433 K; t = 4 hr	DPU: 99.2	MPC: 97.2	—	(Gao et al., 2009a)
PbO/γ-Al ₂ O ₃	DMC	DPU	MPC	P = 1 MPa; T = 433 K; t = 4 hr	DPU: 98.2	MPC: 95.0	—	(Gao et al., 2009a)
NiO	MeOH	NH ₃	MC	P = 5 MPa; T = 473 K; t = 12 hr	—	MC: 21	MC: 98	(Li et al., 2011)
V ₂ O ₅ /TBAB	MeOH	NH ₃	MC	P = 5 MPa; T = 453 K; t = 6 hr; w/ TMM (as dehydrant)	—	MC: 63	MC: 96	(Li et al., 2011)
V ₂ O ₅	MeOH	NH ₃	MC	P = 5 MPa; T = 473 K; t = 12 hr	—	MC: 25	MC: 98	(Li et al., 2011)
V ₂ O ₅	EtOH	NH ₃	EC	P = 5 MPa; T = 473 K; t = 12 hr	—	EC: 11	EC: 99	(Li et al., 2011)
V ₂ O ₅	<i>n</i> -PROH	NH ₃	BC	P = 5 MPa; T = 473 K; t = 12 hr	—	BC: 14	BC: 99	(Li et al., 2011)

^aTBAB: tetrabutylammonium bromide; TMM: trimethoxymethane.^bMPC: methyl N-phenyl carbamate; DMC: dimethyl carbonate; DPU: *N,N'*-diphenyl urea; NMA: *N*-methyl aniline; MC: methyl carbamate; EC: ethyl carbamate; BC: butyl carbamate.

V_2O_5 as a catalyst without dehydrant, as described in Eq. (33).

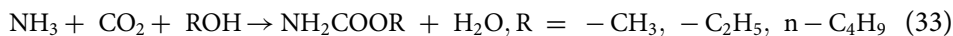


Table 6 presents the performance of the catalytic CO_2 reactions for synthesis of carbamates such as MPC. For the carbamate synthesis, the reaction rate should increase as the acidity of the alcohol decreases. Gao et al. (2009a) found that the lead compounds such as PbO , $PbCO_3$, and $2 PbCO_3 \cdot Pb(OH)_2$ exhibited the excellent catalytic activity for the synthesis of MPC through the reaction of DMC and N,N' -diphenyl urea under pressure. In addition, V_2O_5 catalysts exhibited good catalytic activity for the production of alkyl carbamates using NH_3 , CO_2 , and alcohols (Li et al., 2011). The selectivity of MC, EC, and BC under the pressure of 5 MPa at 473 K was 98%, 99%, and 99%, respectively. Furthermore, the use of a dehydrating agent such as tetrabutylammonium bromide (TBAB) can be effectively to promote the yield of carbamates, especially when sterically hindered amines are used as a starting compounds (Ion et al., 2008).

5.4. Synthesis of DMC from methanol

A number of organic carbonates, such as ethylene carbonates, polycarbonates, and DMC can be used as a carbonylation reagent for several organic transformations. DMC is a carbonyl ester with the formula $(CH_3O)_2CO$, which is a nontoxic, non-corrosive and environmentally-friendly organic carbonate. In a variety of chemical industries, it is used as a solvent (Litaïem and Dhahbi, 2012), an additive in gasoline and diesel (Rajesh Kumar and Saravanan, 2016), and an electrolyte in lithium batteries (Berhaut et al., 2015; Gao et al., 2015a). DMC has a low dielectric constant ($\epsilon = 3.12$), a weak viscosity, and a high biodegradability, and is often used as a solvent in many applications. Moreover, it can be used as a building block for various organic chemicals such as polycarbonates (Anthofer et al., 2014).

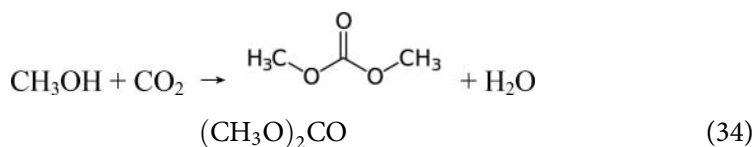
Several reaction routes are available for DMC production; they include (1) direct synthesis from CO_2 and methanol, (2) urea methanolysis, (3) transesterification of EC with methanol, (4) oxidative carbonylation of methanol, and (5) methanolysis of phosgene. The first method is the most attractive one because inexpensive raw materials are used and corrosive reagents such as phosgene and dimethyl sulphate are not used (Saada et al., 2015), as shown in Eq. (34). However, activation of stable CO_2 and thermodynamic limitations are major obstacles to direct synthesis of DMC (Kumar et al., 2017). Therefore, the direct synthesis of DMC from CO_2 and methanol is normally performed at a high pressure in an autoclave reactor. Aside from the CO_2 conversion, several side reactions occur with the direct DMC synthesis, and water is formed as a by-product which will eventually deactivate the catalyst. As a results, both the methanol conversion and DMC yield are still too low to be incorporated in an industrial scale synthesis. To overcome the aforementioned

Table 7. Performance of heterogeneous catalyst for direct synthesis of DMC.

Catalyst ^a	Support ^a	Press (MPa)	Temp (K)	Time (hr)	Conversion (%)	DMC yield (%)	DMC select. (%)	Reference
Mo/Cu-Fe	Silica	0.6	393	—	MeOH: 7.0	6.1%	87.7	(Zhou et al., 2013)
Rh	Silica	0.1	393	0.67	MeOH: ~38	—	~46	(Almusaiteer, 2009)
Rh	ZSM-5	0.1	393	0.67	MeOH: ~44	—	~64	(Almusaiteer, 2009)
Rh-K	Al ₂ O ₃	0.1	353	0.67	MeOH: ~15	—	~15	(Almusaiteer, 2009)
Rh-Ce	Al ₂ O ₃	0.1	353	0.67	MeOH: ~38	—	~1	(Almusaiteer, 2009)
Cu-Ni	Graphite	1.2	378	—	MeOH: 10.1	9.0%	88	(Bian et al., 2009)
CeO ₂	(2-CP)	3	343	2.5	MeOH: 12.4	—	96.3	(Stoian et al., 2017)
CeO ₂	(2-CP)	3	393	2.5	MeOH: 92.0	—	>99	(Stoian et al., 2017)
CeO ₂ -CaO	—	15	393	24	CO ₂ : 2.33	2.961 mmol	—	(Kumar et al., 2017)
Cs-DTP	HMS (IL)	15	323	5	MeOH: 11.9	—	25.8	(Kabra et al., 2016)
CHT	HMS (IL)	15	323	5	MeOH: 9.2	—	82.0	(Kabra et al., 2016)
Ce-Zr oxide	Graphene	27.5	383	16	MeOH: 58.0	33.0%	—	(Saada et al., 2015)

^a2-CP: 2-cyanopyridine as dehydrating agent; HMS: hexagonal mesoporous silica; CHT: calcined hydrotalcite; IL: ionic liquid as promoter.

hurdle, novel catalysts with high a catalytic performance are required.



Various metal oxide catalysts, such as CeO₂, ZrO₂, V₂O₅, TiO₂, and SnO₂, have been developed and evaluated for their efficiency and effectiveness in the DMC synthesis. Different support materials, such as silica, molecular sieve, graphene oxide, activated carbon and multi-walled carbon nanotubes, can be used to increase the stability of the catalyst and the dispersion of the active components. Table 7 summarizes the performance of direct DMC synthesis methods using different catalysts. The methanol conversion and DMC yield are strongly affected by the reaction temperature and pressure, although high pressures are not always necessary for an effective synthesis of DMC. For DMC synthesis, the catalytic activity on both basic and acidic sites is required (Kumar et al., 2017). In other words, mixed oxides catalysts would exhibit higher chemical stability and greater basic-acidic sites, as compared to single metal oxide.

Saada et al. (2015) developed a novel Ce-Zr oxide/graphene nanocomposite as a heterogeneous catalyst for the synthesis of DMC. The maximum methanol conversion and DMC yield at 27.5 MPa and 383 K were found to be 58% and 33%, respectively. The reaction pressure of 27.5 MPa was related with the supercritical state of CO₂. With the Zr and/or Ce catalysts, even though the DMC selectivity

could be high (almost 90% in some cases), the methanol conversion was still limited by the reaction equilibrium (Stoian et al., 2017). To carry an effectively promotion on the DMC selectivity even at a low reaction pressure, incorporation of a dehydrating agent such as 2-cyanopyridine (2-CP) was required.

5.5. Conversion of CO₂ to other organic chemicals

Great progress has been made on catalytic reduction of CO₂ to produce other kinds of value-added chemicals via the construction of C–C, C–H, C–O, and C–N bonds; for example, aromatic aldehydes, organic carbonates, N-containing compounds, and carboxylic acid and their derivatives (Yang et al., 2016). CO₂ can be used as a carbonyl or carboxyl reagent for the synthesis of aromatic aldehydes and carboxylic acids through the construction of C–C bond. Carboxylation making a C–H bond with CO₂ also is an important route for synthesis of carboxylic acids and their derivatives at an ambient temperature and pressure. C–O formation reactions, in which CO₂ is used as a C1-building block, include (1) cycloaddition of CO₂ with epoxides, (2) carboxylative cyclization of propargyl alcohols with CO₂, and (3) carboxylative cyclization of propargyl alcohols with CO₂ to α -alkylidene cyclic carbonates. For synthesis of N-containing chemicals, the C–N bond can be constructed via (1) reactions of CO₂ with various amines, and (2) N-formylation reaction of amines using CO₂ in the presence of hydrogen source, which is a cleaner production of formamides. Furthermore, CO₂ also can be used for different purposes; for instance, methylation of aromatic C–H bonds using CO₂ and H₂ with the assistance of a ruthenium triphos catalyst (Li et al., 2014c).

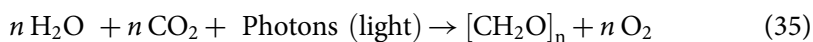
Formaldehyde (HCHO), known as methanal, is an important basic chemical used for manufacturing polymers, as well as synthesis components for complex molecules. It is usually used as an aqueous solution of 37% (w/w), also known as formalin. At present, more than 30 Mt of formaldehyde, in the form of formalin, is annually produced worldwide via methanol oxidation (TECI, 2013). Direct synthesis through hydrogenation of CO₂ to produce formaldehyde is an attractive option since CO₂ is used as a C1 feedstock (Böhme, 2016), although it is still at a conceptual stage. The catalytic reduction of CO₂ to formaldehyde is rarely reported. Nonetheless, several studies have applied a density functional theory for simulating the reaction mechanisms of the reduction of CO₂ to formaldehyde via catalyst, such as Ru/Fe/Os complexes (Dong et al., 2016). In practice, Metsänen and Oestreich (2015) developed the tethered Ru–S complexes for chemoselective hydrosilylation of CO₂ to formaldehyde, where the revealed selectivity of formaldehyde was up to ~18%. In addition, Bontemps et al. (2014) developed a polyhydride ruthenium complex, i.e., RuH₂(H₂)₂(PCy₃)₂, to catalyze the reduction of CO₂. The maximum selectivity of formaldehyde under an atmospheric pressure was approximately 22% (Bontemps et al., 2014).

5.6. Summary

CO₂ can be valorized as a building block for the production of numerous organic chemicals, such as urea, carbamates, dimethyl carbonates and formaldehyde, via the construction of C–C, C–H, C–O, and C–N bonds. The incorporation of CO₂ into polymers is also a promising way to valorize CO₂. Great progress on catalytic reduction of CO₂ to produce aromatic aldehydes, organic carbonates, N-containing compounds, and carboxylic acid and their derivatives has been observed. To establish a sustainable carbon economy system, the future research should focus on designing the optimized process with novel catalysts to facilitate the commercialization of CO₂ transformation to value-added chemicals.

6. Biological CO₂ utilization technology

Biological CO₂ fixation involves the utilization of biological media, such as photosynthetic autotrophic organisms and plants, for CO₂ sequestration via photosynthesis process. The photosynthesis reaction can be described as Eq. (35) (Zhao and Su, 2014). For instance, the glucose (C₆H₁₂O₆) and O₂ can be formed from water and CO₂ in the presence of light ($n = 6$), where inorganic carbon is converted to organic carbon. Approximately 1.8 kg of CO₂ can be fixed through photosynthesis to produce 1 kg biomass of microalgae (De Bhowmick et al., 2014).



To enhance the CO₂ fixation by biomass, biological CO₂ utilization technologies are developed; aquatic or terrestrial biomass is grown on flue gas CO₂ under non-natural photosynthetic conditions. For instance, direct use of CO₂ in flue gas by microalgae has recently been of great interest since they not only consume CO₂ but also can be converted to biofuels or biochemicals. According to a life-cycle assessment (Adom et al., 2014), these bioproducts can reduce GHG emissions by 39–86%, compared to their fossil counterparts. Apart from its environmental benefits such as the carbon neutral property, the production of bio-chemicals by biorefineries using CO₂ (or biomass) is one of the imperative components towards a green economy for green growth society. It was estimated that biotechnologies could contribute to 2.7% of GDP in 2030 within the OECD region, where the largest economic contributions are made in industry and primary production (OECD, 2009). In the following section, the principles and applications of the microalgae technology for CO₂ valorization are discussed.

6.1. Marine biomass options

Marine biomass such as phytoplankton can sequester a large quantity of atmospheric CO₂ (Jones and Otaegui, 1997). Whether they die or are consumed by a higher hierarchy in the food chain, the carbon element remains ultimately

descends into the deep ocean (Farrelly et al., 2013). The biological sequestration of CO₂ by photosynthetic organisms in the upper ocean is only limited by the availability of nutrients in water. As a result, a concept called ocean nourishment was proposed, in which the necessary nutrients are provided to enhance the production of phytoplankton in the ocean (Shoji and Jones, 2001). On the other hand, however, this might change plankton structures which could pose long-term impacts on the ocean eco-system. At the same time, large quantities of produced organic mass sinking to the bottom of the ocean could trigger the production of methane. Thus, this would diminish the beneficial effect of carbon fixation (Stewart and Hessesami, 2005).

Microalgae are ubiquitous and important microscopic organisms in the marine ecosystem as they transform a large quantity of inorganic compounds into biomass. Microalgae are fast-growing organisms and are driven by the same photosynthetic process adopted by higher plants. Since they are rich in protein and organic compounds, they were recognized as a third-generation source of biofuels. They can be converted to biofuel using a variety of methods such as transesterification (as liquid fuel), esterification (as liquid fuel), fermentation (as gaseous fuel) and anaerobic digestion (as gaseous fuel) (Razzak et al., 2013). Microalgae comprise bacteria and cyanobacteria, diatoms (e.g., Chromalveolata), protists (e.g., Chromista), and unicellular plants (e.g., Chlorophyta) (Klinthong et al., 2015).

The energy yield potential of the biomass is a function of productivity, dominant algal species, chemical composition, and harvestability (Mehrabadi et al., 2016). Typically, the lipid content of microalgae per dry-weight is higher compared to those of other plants (Trivedi et al., 2015). However, the product yields (productivity) of microalgae have a few thermodynamic and stoichiometric constraints; the maximum theoretical energy conversion of the full sunlight spectrum into organic matters is roughly 10% (Trivedi et al., 2015). Despite the constraints, microalgae are superior in terms of biomass yield (i.e., 50–70 Mt ha⁻¹ yr⁻¹ in open ponds and 150 Mt ha⁻¹ yr⁻¹ in photobioreactors), as compared with terrestrial energy crops (i.e., ~3 Mt ha⁻¹ yr⁻¹ for soybeans, ~9 Mt ha⁻¹ yr⁻¹ for corn, and ~13 Mt ha⁻¹ yr⁻¹ for switch grass) (Adesanya et al., 2014). Like plants and crops, microalgae require the similar basic elements such as light (radiation), CO₂, water and inorganic nutrients (e.g., N). Therefore, environmental factors such as light intensity, pCO₂, pO₂, pH, and temperature play an important role in microalgae growth and productivity.

6.2. Microalgae technology

Microalgae are photosynthetic microorganism and typically grow suspended in water. They can convert CO₂ into carbon-rich lipids via only one or two steps. In addition, microalgae are genetically amenable to exploitation for both biomass production and carbon sequestration (Mitra and Melis, 2008). Therefore, microalgae technologies are considered as a promising solution for CO₂ fixation while

generating value-added product (Harun et al., 2010); for example, (1) bioenergy: hydrogen, diesel, ethanol and biogas; (2) food supplements: carbohydrates, protein, oils and fats; and (3) bio-chemicals: colorants/pigments, perfumes, and vitamins. The final biofuels can be fed into diesel and/or combined heat and power engines. In this case, actual energy conversion efficiency can be calculated in terms of heat and electricity (Ventura et al., 2013). Aside from that, microalgae can be used as an *in situ* embedded environmental monitors. Since they are quite sensitive to a change in their chemical environment, they can easily sense one and initiate an adaptation of their chemical composition (Ogburn and Vogt, 2017). In general, they exhibit several advantages over terrestrial plants; for example (1) efficient photosynthesis using CO₂ as their main building blocks, (2) fast growth rate, (3) wide tolerance to extreme environments, and (4) potential of growing in intensive cultures.

6.2.1. Direct use of flue gas for microalgae

Microalgae cultivation is one of the technological hurdles since it accounts for one third of the total cost involved in the algal-biofuel production process (Kumar et al., 2015). Direct use of flue gas can reduce the cost of pretreatment. Microalgae also may be grown on flue gases emitted from industries such as iron/steel, paper pulping, and petrochemical industries. Depending on the types of fuels and processes involved, flue gases may contain varying levels of N₂, O₂, CO₂, CO, NO_x, SO_x, H₂O, and dust. The presence of SO_x in feed gas greatly inhibits the growth of microalgae (Yen et al., 2015a). Numerous microalgal strains stop growing at only 50 ppm of SO₂ (Yanagi et al., 1995). For NO_x in flue gas (the major constituent of which is nitric oxide), it can be effectively used as nutrients for microalgae (Farrelly et al., 2013). The typical C:N ratio in the algal cells ranges from 6 to 8 (Kumar et al., 2014). If wastewater is used for cultivation, the C:N ratio of wastewater is generally about 3. Therefore, limitation on carbon source supply would be one of the main constraints to algal production using wastewater (Mehrabadi et al., 2017). In this case, additional CO₂ delivery is imperative for maintaining a sufficient carbon source.

CO₂ delivery as well as control of the pH in culture media are important task forces. Several factors, such as type of mixing and sparger, liquid velocity, and contact time, would affect the mass transfer between gas and liquid phases. An elevated concentration of CO₂ in the gas stream typically increases biomass productivity, while biomass productivity reduces at a high CO₂ level (e.g., above 20% for a range of microalgae strains (Chiu et al., 2009)). In high-rate ponds, a supply of concentrated CO₂ (at least 5%) is sufficient to sustain algal growth (Putt et al., 2011). The rate of CO₂ dissolution into solution media increases with an increase in the pH of the solution. However, it should be noted that an excess of both pH and dissolved CO₂ in an open pond would significantly reduce biomass concentration and productivity, especially in the summer time (Jimenez, 2003). Since the absorbed CO₂ in an open pond tends to be desorbed to the atmosphere, the pond must be operated at a higher pH and lower alkalinity. For the actively

growing algal cells, the optimal pH to provide sufficient CO₂ mass transfer rate ranges between 7 and 8, where bicarbonate is the dominant alkalinity species in the solution (de Godos et al., 2014; Gonzalez-Lopez et al., 2012). The presence of SO_x and NO_x in flue gas also would affect the pH of the media, thereby influencing the CO₂ delivery and biomass productivity.

6.2.2. Open pond systems for cultivation

For large-scale microalgae cultivation, open pond systems have been extensively used due to their simple construction and easy operation. They can offer a greater CO₂ fixation capacity due to their greater culture volume per unit land area (100–300 L m⁻²), as compared to tubular reactors (8–40 L m⁻² for 1–5 cm tubes) (Weissman et al., 1988). Four types of open ponds are commonly used: (1) big shallow ponds, (2) tanks, (3) circular ponds, and (4) raceway ponds. Among them, microalgae cultivation in a raceway pond is the most promising technology, especially in a large scale (Kumar et al., 2015).

For algal growth, light is an important limiting factor. The CO₂ fixation rate by microalgae is related to light utilization efficiency and to cell density (Chiu et al., 2008). Typically, a maximum algal growth rate could be obtained at the light saturation point. Beyond this point, algal growth would be inhibited, which is called photo inhibition. The depth of an open pond should be designed based on the irradiance spectra which are determined by measuring the irradiance attenuation coefficient as a function of wavelength for each strain (Murphy et al., 2015). Although the shallow configuration of a raceway pond can effectively prevent light limitation inside the culture, a large land footprint, when it is scaled up might limit its wide-spread application.

In addition, controlling temperature fluctuation in an open raceway pond is important but challenging work since temperature regulates cellular, morphological and physiological responses of microalgae (Zeng et al., 2011). Temperatures also are related to the rate of water loss through evaporation during cultivation of microalgae. The productivity of microalgae increases with the increase of pond temperature up to an optimum level. Too much increase in the temperature above the optimum would increase algal-respiration and photo-respiration, eventually reducing overall productivity. The optimal temperature for growth of mesophilic microalgae with a high CO₂ tolerance is typically in a range of 286–318 K (Farrelly et al., 2013). For most of the green algae species as well as a few brown, red, blue-green algae species, the optimal temperature ranges for growth are 293–303 K at a light irradiance of 33–400 μmol m⁻² s⁻¹ (Singh and Singh, 2015). Other studies suggest that the optimal growth temperatures of microalgae are 298–308 K, with the maximum cell density obtained at around 303 K (Kumar et al., 2010). On the other hand, the optimal CO₂ concentration for most microalgal species should range between 0.038% and 10% (Zhao and Su, 2014).

Determination of an appropriate open pond system for cultivation relies on land availability, the types of microalgae species, local climatic conditions, and costs of

feedstock and materials such as water (Borowitzka, 1999). Currently, Most microalgal ponds are not economically viable, especially on a large scale due to the following limitations to the system: (1) expensive installation cost, (2) requirement of a large surface area and a land footprint, (3) high water demand, and (4) requirement for a highly trained end-user (CORDIS, 2013). For a raceway pond, typical process hurdles incurring high harvesting costs are (1) poor mass transfer between gas and liquid phases, (2) high risk of culture contamination, (3) low final biomass concentrations, and (4) lack of temperature control (Posten, 2009). In addition, it is challenging to keep cultures axenic in a raceway pond compared to using photobioreactor (PBRs). Regarding the environmental and ecological impacts, the algal production unit may have potential leaks of effluent, thereby causing eutrophication of surrounding waters (Farrelly et al., 2013).

6.2.3. Performance evaluation and key operating factors

For most algae in open pond systems, there are both external and internal factors significantly affecting algal growth, biomass accumulation and production. These factors can be categorized into four types: (1) environmental parameters such as location of a cultivation system, rainfall, and solar radiation, (2) engineering parameters such as pond depth, CO₂ delivery system, power consumption, and composition of feed flue gas, (3) hydrodynamic parameters such as methods of mixing, interphase mass transfer and turbulent flow, and (4) parameters affectively growth algal such as light availability (light/dark cycles), pH, O₂ accumulation, salinity, and algal predators. Table 8 presents the biomass performance of microalgal-based CO₂ fixation and valorization. The ability of microalgae to convert CO₂ to biomass varies by species and culture conditions. In general, the major limiting factors for microalgal growth of microalgae are light availability and interphase mass transfer (Gao et al., 2015b). Therefore, for the design and operation of PBRs, the most challenging factors are efficient mixing, efficient CO₂ delivery, and avoidance of the O₂ accumulation (Weissman et al., 1988). Another key design factor for PBRs with mixing-induced light/dark cycles is the incorporation of a mechanism to periodically transport cells between light and dark regions of the reactor (Gao et al., 2015b).

Vertical mixing is considered as the most significant factor affecting the performance and operating costs of raceway pond. In a PBR system, the mixing process usually accounts for ~69% of total utility costs (Hreiz et al., 2014). Sufficient mixing supplied for a PBR can ensure (1) periodic exposure of cells to sunlight for achieving better light utilization efficiency, (2) keeping cells in suspension, (3) availability of the nutrient to algal cells, and (4) better gaseous mass transfer for CO₂ dissolution and dissolved O₂ removal (Chiaromonti et al., 2013; Kumar et al., 2015; Prussi et al., 2014). The commonly used methods of supplying mixing for a PBR are pumping, mechanical stirring and gas injection (Kumar et al., 2010). According to the environmental conditions (e.g., night/day period, seasonal change), the mixing intensity should be adjusted.

Table 8. Biomass performance on microalgae-based CO₂ fixation and valorization.

Category	Strain	System ^a	Temp (K) ^b	CO ₂ Conc. (%)	Q _g (vvm) ^b	pH _i ^b	X _g (g/L) ^b	μ _{max} (1/day)	P (g/L/day) ^b	f (g/L/day) ^b	Reference
Microalgae	<i>N. oculata</i>	PBR (L = 30; D = 7)	299	2	0.25	7.8	0.01	0.57	0.48 ± 0.03	6.33	(Chiu et al., 2009)
Microalgae	<i>N. oculata</i>	PBR (L = 30; D = 7)	299	5	0.25	7.7	0.01	—	0.44 ± 0.04	7.02	(Chiu et al., 2009)
Microalgae	<i>N. oculata</i>	PBR (L = 30; D = 7)	299	10	0.25	7.3	0.01	—	0.40 ± 0.07	10.50	(Chiu et al., 2009)
Microalgae	<i>N. oculata</i>	PBR (L = 30; D = 7)	299	15	0.25	7.0	0.01	—	0.37 ± 0.02	11.79	(Chiu et al., 2009)
Microalgae	<i>Chlorella sp.</i>	PBR (L = 30; D = 7)	299	2	0.25	7.6	0.10	0.61	0.55 ± 0.08	7.83	(Chiu et al., 2008)
Microalgae	<i>Chlorella sp.</i>	PBR (L = 42; D = 6.5)	291	15	0.1	8 ^c	0.15	0.38	0.27	0.50	(Zhao et al., 2015)
Microalgae	<i>Isochrysis sp.</i>	PBR (L = 42; D = 6.5)	291	15	0.2	8 ^c	0.30	0.18	0.11	0.19	(Zhao et al., 2015)
Microalgae	<i>Synechocystis sp.</i>	PBR	303	—	—	8.5	—	2.4	—	—	(Nguyen and Rittmann, 2016)
Microalgae	<i>S. obliquus</i>	PBR, batch	301	2.5	0.4	6.2	—	—	0.55 ± 0.03	0.96	(Ho et al., 2013)
Microalgae	<i>S. obliquus</i>	PBR, semi-batch	301	2.5	0.4	6.2	4.0	—	0.88 ± 0.03	1.55	(Ho et al., 2013)
Microalgae	<i>S. obliquus</i>	PBR, continuous	301	2.5	0.4	6.2	3.0	—	0.88 ± 0.01	1.53	(Ho et al., 2013)
Microalgae	<i>Chlorella sp.</i>	PBR (L = 80; D = 6), AWW	299	2	0.2	6.0	0.3	0.49	1.30	2.33	(Kuo et al., 2016)
Microalgae	<i>Scenedesmus sp.</i>	PBR (L = 30; D = 8), DWW	298	2.5	0.5	6.8	1.37	0.51	0.20 ± 0.01	0.37 ± 0.01	(Nayak et al., 2016)
Microalgae	<i>Scenedesmus sp.</i>	PBR (L = 30; D = 8), DWW	298	0.038 (air)	0.5	8.4	0.89	0.44	0.13 ± 0.01	0.24 ± 0.01	(Nayak et al., 2016)
Microalgae	<i>Chlorella vulgaris</i>	Raceway ponds (d' = 20)	298	0.038 (air)	0.12	— ^c	0.19	—	~0.026	—	(Murphy et al., 2015)
Cyanobacteria	<i>S. platensis</i>	Raceway ponds (d' = 20)	298	0.038 (air)	0.12	— ^c	0.19	—	~0.051	—	(Murphy et al., 2015)
Cyanobacteria (alkalihalophilic)	<i>Euhalothece ZM001</i>	Tissue-culture flasks (1.0 M NaHCO ₃ /Na ₂ CO ₃)	313	—	—	9.5 ^c	0.07	1.57	1.87	—	(Chi et al., 2013)

^aPBR: photobioreactor; d': depth (cm); L: length (cm); D: diameter (cm); AWW: aquaculture wastewater; DWW: domestic wastewater.

^bTemp: cultivation temperature; Q_g: gas flow rate (vvm as V_{air}/V_{culture}/min); pH_i: initial pH value of culture; μ_{max}: maximum specific growth rate; X_g: biomass concentration; P: biomass productivity; f: CO₂ removal rate.

^cpH without control.

Beside the mixing, controlling O_2 concentration, pH and conductivity of the culture is important to obtain a high biomass concentration and productivity (Jimenez, 2003). Oxygen is a by-product generated from the algal photosynthesis, i.e., approximately 1.9 kg of O_2 is generated per kg of the algal biomass synthesis (Kumar et al., 2014). An excess of dissolved O_2 of in a PBR during algal cultivation would severely damages the algal cells by photooxidation and photoinhibition due to respiration, thereby leading to a reduction in biomass productivity. It was noted that an increase in dissolved O_2 concentration greater than 25 mg L^{-1} would have a negative impact on the microalgae productivity (Jimenez, 2003). Therefore, rapid removal of accumulated O_2 concentration from the system is much critical than CO_2 supply. It is noted that the maximum dissolved O_2 concentration for a 100-m^2 surface and a 20-cm depth pond should be $14.5\text{--}19.0 \text{ mg L}^{-1}$ at a mixing velocity of $3.7\text{--}30.0 \text{ cm s}^{-1}$ (Weissman et al., 1988).

6.3. Concomitant wastewater bioremediation and CO_2 biofixation

Biological treatment process is considered as an efficient approach to simultaneous treatment of wastewater and CO_2 emission since it does not require large energy input and is easy to operate (Passos et al., 2015). Domestic wastewater contains sufficient amounts of carbon, nitrogen, phosphorus and other minerals, which could cause eutrophication and other environmental issues. However, these elements and nutrients can be used as a cheap substrate for the microalgae cultivation in domestic wastewater treatment (Wang and Lan, 2011). Therefore, domestic wastewater treatment based on microalgae raceway ponds has been studied for many decades as a cost-effective alternative to conventional activated sludge systems. Beside domestic wastewater, different types of wastewater such as swine wastewater (Chiu et al., 2015), piggery wastewater (Kuo et al., 2015), and aquacultural wastewater (Kuo et al., 2016) can also be used for microalgae cultivation.

For microalgae cultivation, a large volume of water and trace nutrients such as nitrogen, phosphorous and other elements are required. According to Yang et al. (2011) approximately 3.73 tons of freshwater (without water reuse), 0.33 kg of nitrogen, and 0.71 kg of phosphorus are required to produce 1 kg of biodiesel using the microalgae technology. In addition, using wastewater or seawater as a culture medium could decrease $\sim 90\%$ water requirement and eliminate the need of all the nutrients except phosphate (Yang et al., 2011). For this integrated system, two mechanisms are mainly involved in removal of pollutants from wastewater: (1) direct and/or indirect transformation of pollutants by microalgae via nutrient assimilation and precipitation, and (2) enhanced biodegradation of pollutants using O_2 generated through microalgae photosynthesis. In other words, an “algae–bacteria” symbiosis can take place in a single system. In this case, no additional aeration process, unlike conventional activated sludge reactors, is needed (Passos et al., 2015). Typically, mechanical aeration is the most energy-intensive process in

an activated sludge system, ranging from 60% to 80% of the total energy consumption (Chachuat et al., 2005).

Microalgae can assimilate inorganic chemicals and nutrients in wastewater for growth, thereby reducing nitrogen, phosphorus, heavy metals and other inorganic pollutants in wastewater. Microalgae could bioremediate ammonium, nitrate, phosphate and chemical oxygen demand efficiently from wastewater by 70–98% (Nayak et al., 2016), depending on wastewater composition and weather conditions (Passos et al., 2015). It also was observed that the antibiotics in wastewater can be removed by microalgae, e.g., tilmicosin removal efficiency of 99.8% by *Chlorella* PY-ZU1 (Cheng et al., 2017).

6.4. Integration with anaerobic digestion for hydrocarbon production

Microalgae were considered a promising feedstock for production of biochemicals because of their high photosynthetic yields, year-round production and ability to grow under different environments such as marine, fresh and wastewaters (Alcántara et al., 2013; Mata et al., 2010). However, the high costs of CO₂ supply and cultivation as well as process hurdles such as axenic microalgae and the uncertain nature of downstream processing have limited its industrial application (Chi et al., 2011; Rawat et al., 2013; Williams and Laurens, 2010). If algae-to-fuel technology is to be successful, biofuels should be produced simultaneously with value-added coproducts (Trivedi et al., 2015). On the other hand, a platform technology integrating microalgae growth with anaerobic digestion (AD) was proposed to improve the economic and energy balance of the overall system (Alcántara et al., 2013). Using residual algal biomass as a substrate, the AD process can produce methane. Moreover, the microalgae-based AD could offer a great potential of recovering essential nutrients, such as N and P, which can offset a significant fraction of the process operating costs (Sialve et al., 2009).

Biogas produced by an AD process consists mainly of CH₄ (55–75%) and CO₂ (25–45%) (Meier et al., 2017). CH₄ is the main constituent of natural gas. Compressed natural gas (CNG) was recognized as an alternative to conventional transport fuels such as gasoline and diesel. Due to the high octane number of CNG (i.e., >110), the compression ratio of engines can increase, thereby resulting in a high thermal efficiency (Yang et al., 2014). Conversion of biogas from an AD process into bio-CNG requires gas purification, known as biogas upgrading, using (1) pressurized water scrubbing, (2) pressure swing adsorption, (3) temperature swing adsorption, (4) amine absorption, (5) membrane, (6) cryogenic method, (7) genosorb, and (8) biofiltration. The purified biogas should contain more than 97% CH₄ and less than 2% O₂ (Yang et al., 2014). As the aforementioned CO₂ catalytic reduction to organic fuels in Section 4.3, CO₂ can be hydrogenated to CH₄ via catalytic Sabatier reaction. Therefore, the AD process can be integrated into a CO₂ valorization process, e.g., hydrocarbon production. According to Rawat et al. (2013), approximately 50% of the initial carbon in microalgal biomass could be hydrolysed

and converted to biogas (i.e., 14% as C-CO₂ and 35% as C-CH₄) regardless of the cultivation mode.

6.5. Summary

Flue gas CO₂ can be valorized to grow aquatic and/or terrestrial biomass under nonnatural photosynthetic conditions, as biological CO₂ utilization technologies. For instance, microalgae technology can convert CO₂ into carbon-rich lipids via only one or two steps, which can subsequently generate high value-added products such as energy, food supplements and bio-chemicals. In addition, wastewater can be introduced in biological CO₂ utilizations so the process can be considered as a less energy-intensive biological treatment. On the other hand, microalgae growth could be integrated with anaerobic digestion to improve the economic and energy balance of the overall system. In fact, using residual algal biomass as a substrate, the anaerobic digestion process can produce methane and offer a great potential of recovering essential nutrients (e.g., N and P), which can offset a significant fraction of operating costs.

7. Perspectives and prospects

CO₂ valorization technologies offer a unique opportunity for sustainable carbon cycle as they utilize the CO₂ emissions to create value-added products for further use. At present, it may not have a huge impact on the overall CO₂ emission mitigation since the market for the CO₂ valorization is still small. In fact, rather than the amount of CO₂ used, the most important consideration in CO₂ valorization is the transition towards a circular economy system. The economics of the CO₂ valorization approach rely on the quality of CO₂ stream and the relevant capture/valorization technologies involved. It was estimated that the CO₂ price in 2050 would be in the range of 100–400 USD per ton CO₂ (Hoel et al., 2009). This could provide the great possibility to create a sustainable carbon economy system. On the other hand, the carbon economy system can be achieved by the development and deployment of an innovative technology for cleaner production, thereby leading to a reduction in the use of materials and energy.

However, the widespread development and deployment of CO₂ valorization demonstration have not been achieved due to several major hurdles such as (1) high capital investment, (2) uncertainties in policies, regulations and technical performance, (3) public acceptance, and (4) concerns about human health and safety and environmental risks. From the technological point of view, none of the CO₂ capture/valorization technologies alone can provide a short- to medium-term solution to reduce CO₂ emissions at a level necessary to stabilize current concentrations. In other words, a portfolio solution must be identified to achieve the most effective CO₂ reduction while minimizing social and economic costs. Here we propose three priority research directions for CO₂ valorization: (1) development of innovative catalysts for simultaneous CO₂ capture and utilization, (2) integrated

CO₂ valorization with alkaline waste stabilization and product utilization, and (3) biological carbon mitigation and utilization. The improvement in process control and heat integration for CO₂ valorization technologies also should be considered to maximize the overall energy efficiency.

7.1. Innovative catalysts for CO₂ valorization and biochemical production

Valorization of CO₂ into alternative transport fuels such as methanol and DME is an important CO₂ valorization option. Beside the organic transport fuels, biochemicals such as urea, formaldehyde, (poly-)carbonates and (poly-)carbamates can be produced via CO₂ catalytic reactions. From the catalyst point of view, Ni-based catalysts are commonly used for CO₂ catalytic reactions because they are relatively cheaper and would not be easily poisoned by CO, compared to the Pt-based catalyst. However, for CO₂ catalytic reactions, both temperature and pressure exhibit a significant influence on reactions in gas phase. In the future research, a novel catalyst with thermal stability, great resistance and high activity should be developed to intensify CO₂ conversion for economical production. For instance, dual function materials containing a CO₂ adsorbent and a methanation catalyst could be effective in adsorbing and converting CO₂ in the flue gas to synthetic methane gas. It involves material types of a catalyst, synthesis method, reactor design, and an economically viable renewable energy source.

7.2. Integrated CO₂ valorization with alkaline waste stabilization and product utilization

An alkaline waste treatment integrated with CO₂ valorization is an attractive approach to direct and indirect reduction of CO₂ emissions from industrial or power plants (Chiang and Pan, 2017a). An accelerated carbonation process not only fixes CO₂ from exhaust gas streams as stable carbonate precipitates but also stabilizes alkaline wastes such as wastewater and solid wastes. Moreover, the potential environmental impacts caused by untreated wastes, such as highly alkaline property and heavy metal leaching, can be eliminated. In addition, the carbonated products can be utilized as high value-added materials in various fields such as construction engineering. In the future research, a novel approach for achieving high CO₂ fixation and low energy consumption for CO₂ mineralization by carbonation of alkaline solid wastes should be important. For instance, mass transfer among gas, liquid and solid phases should be properly intensified with a small land footprint (i.e., an achievable plant size). Meanwhile, reaction heat could be obtained directly from the exhaust gas streams or heat-regenerating systems. In practice, the temperature of flue gas (usually above the dew point) is high enough for carbonation. Heat recovery can not only improve carbonation performance but also reduce energy loss. On the other hand, as supplementary cementitious materials in blended cement, the cement chemistry and enhancement mechanism of utilizing the carbonated products should be systematically elucidated.

7.3. Biological carbon mitigation and utilization

Biological CO₂ mitigation and utilization can offer a great potential in the amelioration of climate change. Using fast-growing biomass such as microalgae, it not only reduces CO₂ accumulations in the atmosphere but also assimilates CO₂ for producing energy products and chemicals such as pigments. These high value-added products can provide an opportunity to cover the costs of algal production. For a successful microalgae technology to obtain a high amount of biomass, careful control of pH, CO₂, and O₂ concentration of the culture is critical. Meanwhile, wastewater can be simultaneously treated using this system. Therefore, the biological CO₂ conversion process presents a sustainable option of CO₂ capture, wastewater treatment, and biochemical production, which would be feasible from an economic standpoint and acceptable from an energy perspective. In the future research, although PBR can be effective in growing microalgae, it needs to keep cultures axenic and minimize loss of CO₂ at a large scale. On the other hand, a more efficient harvesting method should be developed to promote the economics of the microalgae technology. For example, integration of an energy-efficient water treatment process for the culture solution with existing open ponds is an alternative. The provision of sufficient CO₂ and removal of excess O₂, (in)organic acid, and salinity from the culture should be simultaneously achieved.

7.4. Improvement in process control and integration

One of the most urgent research needs for development and deployment of CO₂ valorization technologies is related to the improvement in process control and integration. For the industrial and power plants (even for the wastewater treatment plant), appropriate and effective process controls could greatly contribute to reduction of GHG emissions. It suggests that the model predictive control, one of the advanced techniques for process control, is a powerful approach for evaluating the behavior of representative complex dynamical variables by a mathematical model (mostly a linear empirical model). Model predictive control is a feedback control strategy that predicts the future responses of the system of interest over a finite horizon using a model. Thus, it exhibits the ability of anticipated future events and takes control actions accordingly, ensuring economic and robust operation of CO₂ valorization systems.

On the other hands, process integration is defined as a holistic approach for designing the optimized process, which exploits the interactions between different unit processes to effectively utilize energy and resources, thereby minimizing operating costs. For CO₂ valorization technologies, development of viable heat integration methods is an imperative task to improve the overall energy efficiency and emission profile of an emission source. Pinch analysis should be applied for designing the system to minimize energy consumption and to maximize heat recovery. This work should be systematically considered with heating and cooling systems as well as conventional air pollution control equipment, such as selective catalytic reduction (for nitrogen oxides),

electrostatics precipitator (for particulate matters), and flue gas desulfurization (for sulfur oxides). For instance, the heat from exothermic reactions (such as carbonation) should be reused for other unit processes, e.g., material drying, process heating, and conversion of CO₂ directly to methane (synthetic natural gas). A comprehensive performance evaluation also should be carried out to balance the 3E (engineering, economic, and environmental) performance for a variety of valorization technologies.

Acknowledgments

High appreciation goes to the Ministry of Science and Technology (MOST) of Taiwan (R.O.C.) under Grant Number MOST 107-3113-E-007-002 and 107-2911-I-002-535 for the financial support. H. Kim was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20153010091980).

Funding

Ministry of Science and Technology, Taiwan (ROC) (MOST 107-3113-E-007-002). Korea Institute of Energy Technology Evaluation and Planning (20153010091980).

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