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A Review: CO_2 Utilization

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ABSTRACT

Global warming due to the accumulation of atmospheric CO_2 has received widespread attention in recent years. Although various CO_2 capture technologies have been proposed, using the captured CO_2 from power plants is increasingly popular because of concerns with regard to the safety of underground and ocean CO_2 storage. Various techniques related to utilization of CO_2 from the exhausted gas of power plants are discussed in this article. The existing and under-development technologies for CO_2 utilization in the world are briefly reviewed. Two categories, direct utilization of CO_2 and conversion of CO_2 to chemicals and energy products, are used to classify different forms of CO_2 utilization. Regarding the direct utilization of CO_2, in addition to its use in soft drinks, welding, foaming, and propellants, as well as the use of supercritical CO_2 as a solvent, CO_2 capture via photosynthesis to directly fix carbon into microalgae has also attracted the attention of researchers. The conversion of CO_2 into chemicals and energy products via this approach is a promising way to not only reduce the CO_2 emissions, but also generate more economic value. Since CO_2 is just a source of carbon without hydrogen, a clean, sustainable and cheap source of hydrogen should be developed. This article reviews the literature on the production of biofuel from microalgae cultivated using captured CO_2, the conversion of CO_2 with hydrogen to chemicals and energy products, and sustainable and clean sources of hydrogen, in order to demonstrate the potential of CO_2 utilization.

Keywords: CO_2 utilization; Microalgae; Hydrogen; Chemical; Energy product.

INTRODUCTION

Global warming resulting from the emission of greenhouse gases has received widespread environment and energy attention in the recent years. Among these greenhouse gases, CO_2 contributes over 60% to global warming due to its huge emission amount over 30 Gt CO_2 a year (Albo *et al.*, 2010; IEA, 2012). The CO_2 concentration in atmosphere is now close to 400 ppm which is significantly higher than the pre-industrial level of about 300 ppm (Oh, 2010). To mitigate global warming, Kyoto Protocal urges 37 industrialized nations and European Union to reduce their greenhouse gas emissions to a level of 5.2% on average lower than those of 1990 during the period of 2008 to 2012. However, it has been decided to extend Kyoto Protocol to 2017 or 2020 and the reduction targets are only imposed on European Union (EU) and several other European countries. Copenhagen Accord also requests the global temperature increase be limited to 2°C above the pre-industrial level by 2100. International Energy Agency (IEA) in 2012 pointed out to achieve the ± 2°C goal corresponding to a stable CO_2 concentration at 450 ppm, 43 Gt CO_2 should be reduced to reach 14 billion tons. As a result, several key technologies and strategies are required including the improvement of energy efficiency (43%), renewable energy (28%), CO_2 capture and storage (CCS) technology (22%), etc. (IEA, 2012).

However, since fossil fuels would still be the main sources of energy in the next few decades, it is difficult to reach the target of CO_2 emission even though we are devoting to the improvement of energy efficiency as well as large consumption of low-carbon fuels and renewable energy. Nowadays various technologies have been proposed in order to capture CO_2 effectively and economically, although they are not matured yet for post-combustion power plants (Yu *et al.*, 2012). In addition, public concern remains in the safety of underground and ocean CO_2 storage and the potential locations are still under survey and assessed. As a result, CO_2 utilization using the captured CO_2 from power plants becomes more and more recognized worldwide. It not only reduces CO_2 emission to atmosphere but also generates economic values.

Two categories, direct use of CO_2 and conversion of CO_2 to chemicals, are generally classified in CO_2 utilization. In the past years, CO_2 has been applied in various industries, e.g., soft drink, food, agro-chemistry, welding, foaming, fire-extinguishers, propellant, or as a fluid/solvent in various process like drying-cleaning, separation, water treatment, packaging, etc. Supercritical CO_2 has also been found its

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growing application as a solvent for reactions, separation, synthesis of nanoparticles or composites and polymer modification. Though such applications of CO_2 utilization are existing and feasible, their market scales are small and therefore generate small impact on the overall CO_2 emission. The direct use of CO_2 to cultivate microalgae is interesting and extensively investigated because microalgae can not only consume CO_2 but also be the feedstock to produce biofuel. The conversion of CO_2 to chemicals and energy products that is currently produced from fossil fuels is also promising due to the high potential market and promising benefits. Table 1 shows the CO_2-recycled products with their potential of CO_2 reduction and market scale. Revenue generated from the utilized CO_2 can also offset a portion of the CO_2 capture cost. Moreover, a closed-loop carbon cycle can be built through these processes. However, CO_2 still has certain disadvantages as a chemical reactant due to its inert, non-reactive, and low Gibbs free energy properties. Each potential conversion of CO_2 requires energy input that needs to be determined; therefore, the life cycle assessment of such utilization process or concepts must be applied to ensure a neutral or even negative carbon emission.

DIRECT UTILIZATION OF CARBON DIOXIDE VIA MICROALGAE

CO_2 capture via photosynthesis to directly fix carbon into microalgae is nowadays a promising technology and has been extensively studied. The direct utilization of CO_2 via microalgae exhibits many advantages, although the cultivation of microalgae at an industrial scale is still expensive. For example, microalgae use CO_2 as their main building blocks and grow very fast with doubling their biomass volume in less than 24 h for most species. They show much potential in CO_2 mitigation because 1.8 ton CO_2 can be fixed via cultivating 1 ton microalgae (Acién Fernández *et al.*, 2012). Recent reviews addressed the conversion of CO_2 into biomass via microalgae, the conversion rates of CO_2 were 36 g/m^2/day (Acién Fernández *et al.*, 2012) and 600 g/m^3/day (Farrelly *et al.*, 2013). Accordingly, a land of 50,000 m^2 or a reactor of 3,000 m^3 is required to produce 1 ton microalgae with a conversion rate of 1.8 ton CO_2 for practical application. In addition to the direct fixation of CO_2 via cultivation, the harvested microalgae also show enormous potential in the production of energy, food, chemicals and valuable nutrients. Moreover, the photosynthesis of microalgae accompanies with the precipitation of $CaCO_3$, a potentially long-term and stable storage of CO_2 (Aresta *et al.*, 2005). As a result, these advantages and potentials make microalgae a suitable candidate to solve CO_2 and energy issues because of their potentially high capability of CO_2 mitigation as well as high additional values as biomass in biofuel production. In addition, the net CO_2 emission is assumed to be essentially zero if CO_2 released from the biomass-derived energy can be recycled and reused by cultivation of microalgae.

It is promising to cultivate microalgae directly using the flue gases from fossil fuel power plant, the highest CO_2 emission source, or other industries like steel, cement, and petrochemical industries. Microalgae productivity increases

Table 1. Potential of CO_2 reduction and market scale for CO_2-recycled products.

Product	Reaction	Potential of CO_2 reduction (ton CO_2/ton of product)	Market scale (annual)	Reference
Microalgae	-	1.8	Global demand: 1,350 MT (refer to biodiesel) Market value: $22.2 billion	Tan, 2013
Urea	$2NH_3 + CO_2 \rightarrow [H_2N^-COO][NH_4]$ $[H_2N^-COO][NH_4] \rightarrow NH_2CONH_2 + H_2O$	0.735–0.75	Global production: 198.4 MT Market value: $59.5 billion	Heffer and Prud'homme, 2013
Polycarbonate	CO_2 + Propylene Oxide → Polyethercarbonate	0.5	Global demand: 3.6 MT Market value: $14.4 billion	Tan, 2013
Methanol	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	1.375	Global production: 75 MT Market value: $36 billion	Methanol Institute, 2013
Dimethyl carbonate (DMC)	$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O$ $R_1R_2(OMe)_2 + CO_2 \rightarrow DMC + R_1OR_2$ $R_1OR_2 + 2MeOH \rightarrow R_1R_2(OMe)_2 + H_2O$	1.467	Global demand : 0.24 MT Market value : $280 million	Tan, 2013
Dimethyl ether (DME)	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $CO_2 + H_2 \rightarrow CO + H_2O$	1.913	Global demand: 6.3 MT Market value: $3.2 billion	Tan, 2013

with CO_2 concentration in feed stream; however, the productivity decreases at high CO_2 concentration levels (above 20%) (Farrelly *et al.*, 2013). It is reported that pH significantly affects the physiology of microalgae. Generally, the optimum conditions for the growth of microalgae are at pH 7 and 8, respectively, while most microalgae hardly grow at pH below 4 or above 9. The increase of CO_2 concentration lowers the pH values in the cultivation media and high purity CO_2 gas therefore is not demanded for cultivation of microalgae. Moreover, pH value increases with biomass concentration. As a result, a careful pH management during cultivation especially in the early stages is critical for the growth of microalgae (Farrelly *et al.*, 2013).

As for fossil fuel power plant, the flue gases typically contain not only CO_2 but also CO, NO_x, SO_x, N_2, H_2O and excess O_2. SO_x greatly restrains the growth of microalgae and stops the growth in a level of 50 ppm of SO_x. It is considered that a reduction in pH value in the presence of SO_x rather than the toxicity of SO_x inhibits the growth because the growth is not restrained when pH value is back following by the introduction of NaOH (Matsumoto *et al.*, 1997). NO_x, especially NO, can be an effective nutrient for microalgae. However, it is also reported that the addition of NO and NO_2 at early stage would restrain the growth. This is due to NO_x acts in a similar way to SO_x by decreasing pH value in the media. Temperature is another significant factor in microalgae cultivation. High temperature flue gases usually raise the issue of cooling cost as well as water evaporation during cultivation. As a result, mesophilic microalgae with high tolerance to CO_2 are commonly used in the optimum temperature range of 13–45°C (Farrelly *et al.*, 2013).

Once harvested, microalgae as the biomass can produce lipids, protein and carbohydrates, which can be further utilized to produce energy, food, chemical and nutrient. Microalgae are generally transformed into energy via direct combustion, thermochemical, photochemical or biochemical processes, such as reforming, gasification, pyrolysis, fermentation, transesterification, etc. In addition, the emission of hydrocarbons and carbon monoxide through the conversion of microalgae into energy are largely reduced. SO_x can also be eliminated because microalgae are free of sulphur. Among the various forms of energy, microalgal biofuels are particularly attractive, which are typically generated from conversion of the extracted microalgal lipids (i.e., crude lipids or total fatty acids of microalgae) by transesterification. Until now, the microalgal biofuel production is still not so economical; a major reason is that large energy is consumed in the lipid extraction from algal cells and the transesterification process. Most matured microalgae are composed of water and lipids are generally enveloped by the tough cell wall, thus hindering the oil extraction from microalgae. The efficiency of transesterification reaction depends on the type of catalysts and the operating conditions. For this reason, efficient extraction and transesterification in addition to cultivation and harvest of microalgae are the key processes in microalgal biofuel production. To improve production yield, various extraction methods have been reported including conventional solvent (for example, hexane) extraction, accelerated solvent extraction (using organic solvents at high pressures and temperatures above the boiling point) and supercritical fluid extraction (Cheng *et al.*, 2011; Mouahid *et al.*, 2013).

Supercritical fluids (SCFs) defined as a substance at a temperature and a pressure above its critical point have been widely applied in a variety of physical and chemical processes like extraction, reaction, material synthesis, etc. SCFs possessing gas-like viscosities and extremely low surface tensions allow them to penetrate through cell wall of microalgae, thus making extraction of lipids much easier (Huang *et al.*, 2013). In addition, SCFs can be employed without dewatering of microalgae. Among SCFs, supercritical methanol and ethanol are generally used and capable of simultaneous extraction and conversion of oils from microalgae into biofuels. CO_2 under supercritical or near supercritical condition (P_c = 7.38 MPa, T_c = 31.2°C), considered as a non-toxic, non-flammable, inexpensive and environmentally friendly solvent with tunable properties, is also used as both the medium for oil extraction and the co-solvent coupled with alcohols in transesterification. SCF extraction of microalgal oils is far more efficient and powerful than the traditional separation methods.

In general, microalgae exhibit a number of advantages over other plant feedstock in CO_2 capture and utilization concerned with (1) high photosynthetic conversion, (2) rapid production, (3) high capacity to produce a wide variety of biofuel feedstock, (4) high capability of environmental bioremediation such as CO_2 fixation from atmosphere/flue gas and water purification, and (5) non-competitiveness for land with crops and food. In view of CO_2 mitigation, CO_2 can directly be utilized in both extraction and transesterification processes in which pure CO_2 at supercritical condition is used as solvent and co-solvent, respectively. Moreover, CO_2 can indirectly be applied in the cultivation of microalgae as well, making microalgae a potential alternative to solve energy and environmental issues.

CARBON DIOXIDE TO CHEMICALS

CO_2 is a major greenhouse gas, however it can also be considered as an important carbon source to produce valuable chemicals and fuels via CO_2 hydrogenation, CO_2 cycloaddition to epoxides, CO_2 carbonylation of amines or alcohols, and the like (Dai *et al.*, 2009; Razali *et al.*, 2012). Several innovative technologies as selectively transform CO_2 into highly valuable materials by alternating copolymerization of CO_2 with other organic compounds, have been developed for industrial applications and are accessible to markets. An excellent review by Song (2006) had addressed the barriers, strategic objectives, and approaches for CO_2 capture and utilization. The barriers for CO_2 utilization are as follows: (1) cost of CCS techniques; (2) energy requirement in CO_2 conversion; (3) market scale; (4) socio-economical driving force. The strategies of CO_2 utilization should focus on the use of CO_2 for the environmentally benign process, the production of industrially useful chemicals from CO_2, and the CO_2 recycling involving renewable energy to conserve carbon sources.

In view of thermodynamics of CO_2 conversion, for example, Gibbs free energy of CO_2 and related substances, many reactions exhibit positive change in enthalpy ($\Delta H > 0$) and thus are endothermic. In other words, low energy input, active catalysts, and effective reaction conditions are demanded for conversion of CO_2 to chemicals. One feasible and thermodynamically practical route is to use CO_2 as a co-reactant to react with another substance that possesses higher Gibbs free energy, for example, hydrogen and methanol. Omae (2012) extensively reviewed related products (carbonates) from CO_2 with various types of reactive substances including oxygen-containing compounds, nitrogen-containing compounds, carbon-carbon unsaturated compounds and others substances such as hydrogen. Aresta and Dibenedetto (2007) comprehensively reviewed the interactions and the bonding modes of CO_2 with metal centres of catalysts. Various modes of bonding were generated according to different metal centres of catalyst, thus could drive different reactions based on CO_2 and further resulted in different structural features of compounds. They also reviewed the incorporation of CO_2 as a building block into an organic substrate via the following bondings: (1) C-C bond to afford acids, esters, etc.; (2) C-N bond to afford carbamates and isocyanates; (3) C-O bond to afford cyclic, linear, and poly carbonates.

The use of catalyst is generally required to transform CO_2 to organics under mild conditions. Numerous researches on CO_2 conversion to chemicals over homogeneous and heterogeneous catalysts have been proposed. Both homogeneous and heterogeneous catalysts possess advantages and disadvantages. Homogenous catalysts typically show higher catalytic activity and selectivity than heterogeneous catalysts under mild conditions. Heterogeneous catalysts, however, have superior stability and durability and provide simplicity in separation, handling and reactor design, thus are preferred in CO_2 conversion (Dai *et al.*, 2009; Razali *et al.*, 2012).

Although catalytic process is considered to be popular and potential in CO_2 utilization, several challenges remain to limit the progress. The catalytic CO_2 utilization requires a huge amount of catalysts and a condition at high temperature, high pressure and long reaction time because of chemically stable CO_2, and therefore, restrains the process in a laboratory scale with low conversion. Plasma, another promising technology, having several advantages such as high conversion and selectivity without catalyst and no concern about carbon deposition, has been attracted increasingly in the past decades though the energy use now is still a problem (Tao *et al.*, 2011). Generally, plasma acts like a catalytic role by inducing reactive species required for chemical reactions. Plasma techniques can be classified as thermodynamic non-equilibrium plasma and thermodynamic equilibrium plasma, also simply called cold plasma and thermal plasma, respectively, depending on the plasma temperature corresponding to the level of energy density and electron density (Tao *et al.*, 2011). Cold plasma with a relatively low gas temperature (near room temperature) in contrast to a high electron temperature (over 10,000°C) possesses several advantages including (1) high chemical activity at low gas temperature in the absence of solvents; (2) prevention of the sintering of the generated particle products; (3) capability of an in-situ tuning; (4) readily control of functionalization (Witvrouwen *et al.*, 2012). Cold plasma can be divided into two groups according to the type of discharge: dynamic and static discharge. Generally, gliding arc plasma (GAP), dielectric barrier discharge (DBD) and microwave plasma generate plasma dynamically, while corona discharge generates plasma statically. A high efficiency of as much as 85% has been reported for organic cracking by GAP. Hydrogen production by DBD technique was reported to result in an efficiency of 55%, which was comparable to the existing techniques. However, the energy demand for reaching a plasma state predominantly restricts the plasma process under developing stage (Bičáková and Straka, 2012).

Currently, the synthesis of urea and organic carbonates via CO_2 conversion are the existing chemical processes in chemical industry. Urea is used to produce fertilizers and polymers. More than 90% of worldwide production of urea is used as solid nitrogen fertilizer due to its high nitrogen content (46%). The world urea supply capacity is at 198.4 million metric tons (Mt) in 2013 and is estimated to increase to 236.3 Mt in 2017 (Heffer and Prud'homme, 2013).

From a thermodynamic point of view, organic carbonates are suitable target compounds in the conversion of CO_2 because of three oxygen atoms existing in the molecules. They are of industrial interest nowadays and produced mainly from toxic phosgene (Dai *et al.,* 2009). On account of environment and safety, the replacement of hazardous phosgene route by CO_2 is highly concerned and encouraged. Organic carbonates can be roughly categorized into linear, cyclic and poly carbonates including ethylene carbonate (EC), propylene carbonate (PC), styrene carbonate (SC), dimethyl carbonate (DMC), lexan, etc., which are organic compounds used as raw materials in a wide range of chemical reactions, as precursors to synthesize polycarbonates, as electrolytes in lithium batteries, and as polar solvents (Dai *et al.*, 2009). The synthesis of cyclic carbonates through the cycloaddition of CO_2 to epoxides has been developed and commercialized. This process is promising and considered as a green process because CO_2 is inserted into epoxides without use of phosgene and production of side products. Dai *et al.*, (2009) also reported the recent development of cyclic carbonates and DMCs synthesized from CO_2 using heterogeneous catalysts via various routes. They summarized the production of organic carbonates via the reaction of CO_2 with organic compounds such as epoxides and alcohols on heterogeneous catalysts. Razali *et al.* (2012) reviewed the potential of CO_2 utilization to organic carbonates via heterogeneous catalyst and focused on the properties of heterogeneous catalysts, CO_2 conversion, products yields, reaction conditions, limitation, and reaction mechanisms.

Tan and his coworkers synthesized alternating polycarbonates from the copolymerization of CO_2 with epoxides such as propylene oxide, allyl glycidyl ether and cyclohexene oxide using a yttrium-metal coordination catalyst system (Yttrium trifluoroacetate ($Y(CF_3CO_2)_3$), diethylzinc ($ZnEt_2$) and glycerine). They further combined the prepared polycarbonates with a sol-gel process to generate polycarbonate-silica nanocomposite in which thermal and mechanical properties are well improved as compared to polycarbonate itself (Tan and Hsu, 1997; Hsu and Tan, 2001, 2002, 2003; Tan *et al.*, 2004; Tan and Kuo, 2005).

In general, the utilization of CO_2 to chemicals should follow a sustainable way and could then be a solution to reduce CO_2 emission. However, the amount of the generated chemicals from the utilization of CO_2 is not high enough to consume most of the captured CO_2, for example, only 110 million tons of CO_2 a year are either converted into organic or inorganic compounds (Aresta and Dibenedetto, 2007). As a result, the current production of chemicals from CO_2 though contributes to the global carbon reduction; the contribution is not large enough. Therefore, the conversion of CO_2 to energy products is believed to be an alternative to consume more CO_2.

CARBON DIOXIDE TO ENERGY PRODUCTS

Fossil fuels, though a most valuable gift from nature, were once abundant but nowadays close to exhaustion. Although new resources (e.g., shale gas) have been discovered, these carbonaceous fuels are only available by decades. As a result, we still have to face the problems of serious shortage and increasing price of fuels. To reduce the dependence of fossil fuels, the development of energy products from renewable energy thus are popular recently. The utilization of CO_2 to chemicals that can store energy chemically is a feasible way and has received a great deal of attention. The utilization and recycling of the emitted CO_2 to energy products can not only replace fossil fuels, but also contribute to the global climate change positively. Among these energy products, methanol, dimethyl carbonate (DMC) and dimethyl ether (DME) are the most promising candidates and are highly concerned to chemically stored energy (Rihko-Struckmann *et al.*, 2010; Ganesh, 2011; Omae, 2012; Razali *et al.*, 2012; Olah, 2013). Some physical and chemical properties of these products compared with those of the conventional fuels are shown in Table 2.

Methanol

Methanol has been widely used in medicals, pharmaceuticals, dyes, paints, plastics, rubbers fibers, etc. The global methanol industry, over 90 methanol plants worldwide, has a total production capacity of about 75 million tons and generates an annual sale around US$ 36 billion (Methanol Institute, 2013). Methanol is also an important source as the feedstock to produce DMC and DME. Because the energetic efficiency of methanol is higher than that of its derivatives, thus more research has been focused on the synthesis of methanol. Methanex, the world's largest supplier of methanol, reports that the worldwide requirement of methanol reached to 48 million tons in 2012 and will increase to 85 million tons in 2015. Nowadays about one-third of methanol (annually 25 million tons) is used in production of energy products, which largely motivates the development of global methanol industry; however, only a fraction of methanol is produced using hydrogen generated from renewable resources like wind or solar energy. Considering the shortage of oil, the market of methanol is more potential if it can be used to replace the gasoline consumption in vehicles and its erosion problem can be solved as well. This strategy not only improves combustion efficiency and reduces CO_2 emission (about 45% as compared to gasoline), but also creates much more benefits and values in economics, environment and energy (Steinberg, 2000). The concept to synthesize methanol from the feedstock of CO_2 and water was firstly proposed by Steinberg and Dang (1977) and many similar proposals were proposed as well afterward (Steinberg, 1997; Joo *et al.*, 1999, 2004; Olah, 2005). The concept is further reinforced as the basis of an "anthropogenic chemical carbon cycle" which is also termed the "Methanol Economy" by Nobel Prize Winner George Olah and his coworkers (Olah, 2005).

Industrial production of methanol is being currently carried out by reforming fossil-derived syngas (primary CO and H_2) over metal based catalysts (e.g., Cu-Zn system) at 5–10 MPa and 200–300°C via Eq. (1). Numerous researches focus on the use of CO_2 instead of CO in methanol synthesis according to Eq. (2), even though it is a great challenge due to the high activation of CO_2 and the demand of substantial energy input. In the presence of CO_2, the above reactions can be accompanied by the reverse water-gas-shift reaction (RWGS) (Bos *et al.*, 1989; Aresta and Dibenedetto, 2007; Razali *et al.*, 2012).

Table 2. Properties of CO_2-recycled and conventional fuels.

Item	CO_2-recycled fuels			Hydrogen	Conventional fuels		
Property	Methanol	DMC	DME		Propane	Gasoline	Diesel
C/H/O (mass %)	38/12/50	40/7/53	52/13/35	-	82/18/0	88~85/12~15/0	86/14/0
Boiling Point (°C)	65	90	–25	–253	–42	30–190	180–360
Flash Point (°C)	11	18	–41	–253	–104	–43	> 63
Density (kg/L)	0.79	1.07	0.67	8.9×10^{-5}	0.50	0.75	0.84
Flammability Limits in Air (vol.%)	5.5–36	4.2–13	3.4–17	4–74	0.4–2.1	1.4–7.6	0.6–7.5
Research Octane Number (RON)	100	127	35	> 130	112	90–100	15–25
Cetane Number	5	-	55–60	-	5	-	40–55
High Heating Value HHV (GJ/ton)[1]	22.9	19.6	31.7	142.2	50.2	47.0	45.8
Low Heating Value LHV (GJ/ton)[1]	20.1	13.5	28.9	120.2	46.3	44.0	42.8

[1] GREET, The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model, GREET 1.8d.1, developed by Argonne National Laboratory, Argonne, IL, released August 26, 2010. http://greet.es.anl.gov/.

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^0_{298} = -91\ kJ/mol \qquad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^0_{298} = -49\ kJ/mol \qquad (2)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^0_{298} = +42\ kJ/mol \qquad (3)$$

In view of thermodynamics, the methanol production yield increases with decreasing reaction temperature because of the exothermal methanol formation and endothermic RWGS reaction. However, a high reaction temperature over 240°C is required to activate CO_2 for methanol production due to chemically inert nature and low reactivity. Unfortunately, high temperature operation favors the formation of by-products such as other alcohols or hydrocarbons and thus decreases the methanol selectivity. In view of reaction, selection of catalysts, generation of water and consumption of hydrogen should be concerned. One highly effective catalyst could increase methanol production and avoid undesired by-products formation. The generation of water in both routes decreases methanol production because water acts as an inhibitor to active sites of catalysts. On account of the currently high price of hydrogen, the enormous consumption of hydrogen in methanol production makes the process not of interest in industrial application and constrains the commercialization. The hydrogen issue is discussed below.

An effective catalyst is considered as the key for success of methanol production. The catalysts used in CO_2 hydrogenation are mostly modified from those used in CO hydrogenation. How to improve activity and stability of catalyst has largely been addressed. Razali *et al.* (2012) reviewed various strategies and development in heterogeneous catalyst and demonstrated that the catalytic activity of CO_2 conversion to methanol depends on various conditions: (1) the metal and catalyst structures; (2) the uniformity of metal particle size; (3) the distribution of metal on support; (4) the growth of the metal particle during operation; (5) the surface area of catalysts; (6) the active sites on catalyst; (7) the stability and durability of catalysts; (8) the types of promoters and supporters. Based on these conditions, Cu/ZnO based Al_2O_3 prepared by co-precipitation (Spencer, 1999) has been extensively used and studied for hydrogenation of CO_2 to methanol over the past few decades. Cu is generally selected due to abundant availability coupled with lower cost compared to precious metals. In addition, Cu^+ and Cu^0 species are the crucial catalytic sites leading to high activity and selectivity. The methanol synthesis over Cu has been found to be a structure-sensitive reaction, and the key to high performance is to provide a large accessible Cu surface area (Behrens *et al.*, 2013). However, Cu alone is not enough in methanol synthesis from CO_2 hydrogenation (Chinchen *et al.*, 1986; Fujitani and Nakamura, 2000; Oguchi *et al.*, 2005a, b). Al_2O_3 acts as a refractory oxide and structural promoter to increase the total surface area of catalyst, the distribution of Cu on surface, and the mechanical stability of composite, which can stabilize the Cu/ZnO structure and retard the sintering of Cu particles (Bart and Sneeden, 1987; Chinchen *et al.*, 1988; Toyir *et al.*, 2001b; Wang *et al.*, 2013). However, a negative effect of water was observed due to the hydrophilic nature of the support Al_2O_3 (Bando *et al.*, 1997; Inui *et al.*, 1997; Bonura *et al.*, 2011).

It is generally accepted that ZnO acts as a physical spacer between Cu particles and helps the dispersion of Cu with an optimal Cu:Zn ratio as 70:30 (Behrens, 2009). The crucial atomic structure pattern for Cu/ZnO composite was identified from a combination of experimental evidence and density functional theory calculations by Behrens *et al.* (2012). As a result, the active sites consisted of Cu decorated with Zn atoms could be stabilized by a series of well-defined bulk defects and surface species. However, the functions of ZnO to promote catalytic activity are still in dispute. For example, Bowker *et al.* (1988) mentioned that ZnO could influence adsorptive property of catalyst and contain interstitial hydrogen to at least three monolayers depth. Duprez *et al.* (1990) reported that ZnO transfers oxygen atoms (probably OH groups) to Cu particles during methanol synthesis. Fierro *et al.* (1996) proposed that ZnO plays a role of promoter by affecting the hydrogen reduction of Cu. Choi *et al.* (2001) commented that ZnO acts as support and a dispersing agent that can control the Cu^+/Cu^0 ratio as well as stabilize Cu^+ sites without affecting the Cu morphology. Toyir *et al.* (2001a) made a similar comment on the role of ZnO as support and further mentioned that ZnO involves in the hydrogen flow from the spillover of Cu. Although the role of ZnO is still in dispute to date, the addition of ZnO certainly promotes the dispersion and stability of Cu on the composite, thus leading to high activity.

Other modifiers like ZrO_2, CeO_2 and Ga_2O_3 have been proposed and studied as well. ZrO_2 is a promising support and promoter for catalyst due to its high stability under reducing or reactive atmospheres (Denise and Sneeden, 1986; Gao *et al.*, 2013). ZrO_2 instead of ZnO or the use of CuO/ZrO_2 were found to have better performance than Cu/ZnO (Oguchi *et al.*, 2005a; Szizybalski *et al.*, 2005; Yao *et al.*, 2006). However, the functions of ZrO_2 similar to those of ZnO, were also divergently reported (Jung and Bell, 2002; Oguchi *et al.*, 2005a, b; Gao *et al.*, 2013). CeO_2 acted as support or promoter can also accelerate CO_2 hydrogenation. The oxygen storage function of CeO_2 is the most notable property to affect the valence state of metal oxides and results in the promotion of catalyst (Miki *et al.*, 1990; Oguchi *et al.*, 2005b; Pojanavaraphan *et al.*, 2013). The incorporation of ZrO_2 into the crystalline structure of CeO_2 to form Ce-Zr-O oxides has been extensively investigated recently according to their better thermal stability, smaller crystallite size, and lower coke formation —a major cause of catalyst deactivation (Mamontov *et al.*, 2000; Pojanavaraphan *et al.*, 2013). Ga_2O_3, as a promising promoter according to its redox property (storage and release of oxygen), can induce the strong metal-support interaction between metal and Ga_2O_3 surfaces with facilitated electron transfer, giving a higher activity for methanol production from CO_2 hydrogenation (Toyir *et al.*, 2001a, b; Haghofer *et al.*, 2012; Zhou *et al.*, 2013).

Besides metal-based catalysts, enzymes based materials can also be used in the methanol synthesis from CO_2 and water. Aresta and Dibenedetto (2007) reviewed the processes using a cascade of metal enzymes, in which the electron source, for example, the $NADPH^+/NADP$ couple, is the limiting factor and is necessary for the reduction of CO_2 into methanol. They also mentioned that the cheap reducing agents or solar energy should be used. Omae (2012) reviewed several types of catalysts as well including Cu, Zn, Ni, Al-based ammonia borane ($Al\text{-}NH_3BH_3$), N-heterocyclic carbenes, etc.

Recently, several integrated processes based on the concept of CO_2 mitigation have been developed and their feasibilities have been evaluated as well. The Hydrocarb process as well as the Hynol process were originally designed to produce methanol and clean carbon from any carbonaceous materials such as biomass, fossil fuel, waste, etc. (Steinberg, 1990; Yamada *et al.*, 1992; Steinberg and Dong, 1993). Generally, biomass combined with fossil fuels is processed in the Hydrocarb process, while natural gas instead of fossil fuels is processed in the Hynol process. Both processes basically consist of two major steps, hydrogasification of carbonaceous materials with hydrogen to methane and thermal decomposition of methane. Methanol is catalytically synthesized by CO and H_2 produced in the process. An alternative process so-called Carnol process has been developed (Steinberg and Dong, 1994; Steinberg, 1996) which consists of three parts: (1) capture of CO_2 from flue gas of a coal-fired power plant, (2) a process which converts CO_2 in the presence of H_2 from natural gas to methanol, and (3) the use of methanol as a fuel component in car. Carbon sources are obtained by extracting CO_2 from the stack gases of coal-fired power plants, while hydrogen sources are obtained from thermally decomposing methane (over 900°C). This process is proposed to be technically feasible and economically competitive with alternative CO_2 disposal systems for coal-fired power plants, in which up to 56% of CO_2 emission reduction for the entire system can be obtained (Steinberg, 1997). In general, the Carnol process is regarded as carbon neutral in the sense that all the carbon present in methane ends up as solid carbon without any CO_2 emission. However, such high temperature is a disadvantage when a thermally efficient heat recovery system is demand.

The CAMERE process (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction) was proposed to fix CO_2 by Joo *et al.* (1999), in which a two-step CO_2 hydrogenation process contains a RWGS reactor followed by a methanol synthesis reactor to produce methanol. CO_2 is firstly conversed to CO using $ZnAl_2O_4$ as the catalyst over 600°C in a RWGS reactor. After water removal, CO is then fed in the following reactor to produce methanol using $Cu/ZnO/ZrO_2/Ga_2O_3$ (5:3:1:1) as the catalyst at 300°C and 2.76 MPa. In this two-step process, RWGS reactor is used to adjust CO/H_2 ratio in feedstock, which can reduce the generation of water in the methanol synthesis reactor and consequently increase the production yield of methanol and reduce the gas reflux ratio. In general, this two-step CO_2 hydrogenation has been shown to be superior to the direct CO_2 hydrogenation. However, the catalysts developed so far are not satisfactory in terms of activities and stabilities. Besides, the high cost of hydrogen prevents the practical use of CAMERE process to mitigate CO_2 (Joo *et al.*, 2004).

Netherlands-based BioMCN is the first company to commercially produce and sell industrial quantities of high quality bio-methanol from biomass since 2010 with a production capacity of 800,000 tons a year (Methanol Institute, 2011). The crude glycerine, a by-product from biodiesel production, is converted into bio-methanol by BioMCN process as shown in Eqs. (4) and (5). Although CO_2 is not directly used for methanol production, this commercial production of bio-methanol still shows its potential to substantially reduce CO_2 emissions because biomass can be cultured by CO_2 bio-fixation and its energy can be fully utilized. Moreover, bio-methanol via BioMCN process can avoid the social and environmental issues associated with conventional biofuels such as the "food vs fuel" debate, etc. As reported by Methanol Institute, a 70% reduction of CO_2 in comparison with the conventional methanol production technologies is achieved by BioMCN process.

$$\begin{aligned}&\text{biomass} \xrightarrow{\text{transesterification}} 90\%\ \text{bio-diesel} + \\ &10\%\ \text{crude glycerine}\end{aligned} \tag{4}$$

$$\begin{aligned}&\text{crude glycerine} \xrightarrow{\text{purification}} \text{glyerine} \xrightarrow{\text{steam reforming}} \\ &CO_2 + CO + H_2 \xrightarrow{\text{methanol synthesis}} \text{bio-methanol}\end{aligned} \tag{5}$$

Mitsui Chemical Inc. built a pilot plant of approximately 100 tons a year to directly convert CO_2 into methanol using its own developed catalysts in Osaka. This company currently utilizes its factory exhaust rather than pure CO_2 as the carbon source. In order to expand the hydrogen source, the use of renewable energy such as sunlight to get hydrogen by splitting water is now under development for this process. However, several challenges remain and constrain its commercialization progress such as the lack of long-term operating stability and the huge consumption of electricity and steam.

In Reykjavik, Iceland, Carbon Recycling International (CRI) constructed the facilities in 2010 to utilize CO_2 in flue gas and electricity from a geothermal power plant to make methanol for vehicles and trucks. CO_2 from geothermal power generation is at high concentration, nearly 90%, which is more readily captured as carbon source. Hydrogen is generated via water electrolysis using electricity from geothermal power plant. The amount of methanol production is scheduled to be 4,000 tons a year. This Industrial Scale Plant is also named "The George Olah Renewable Methanol Plant" to honor the Nobel Prize Winner Professor George Olah, because the concept of process design matches the idea "Methanol Economy" advocated by Prof. Olah. In addition, CRI has announced tentative plans to scale up the production to a commercial level of annual 80,000 tons in Northern Iceland which would use the emissions from Landsvirkjun's 60 MW geothermal facility in Krafla. CRI can be regarded as the first company worldwide to produce methanol from CO_2 in a commercial-scale plant.

DMC

DMC is considered as an environmental friendly chemical with several advantages such as biodegradability, low bioaccumulation, low persistence and low toxicity as 1,000 times less than phosgene. Moreover, DMC shows great activity towards nucleophilic molecules (e.g., primary amines and phenols), thus makes it a valuable reactant for the production of other useful organics (Keller *et al.*, 2010). For example, DMC acts as a carbonylation agent to replace the hazardous phosgene in the synthesis of polycarbonate or isocyanate, as well as a methylation agent to replace dimethylsulfate and methylhalides in related reactions (Tundo and Selva, 2002; Cao *et al.*, 2012; Keller *et al.*, 2010). In addition, DMC is widely used as fuel additive to significantly increase the octane number of fuel because of the high oxygen content of DMC (Pacheco and Marshall, 1997). Another promising application for DMC is acting as an alternative solvent or additive according to its strong solvation force. For example, DMC can replace ketones and ester acetates in paints and adhesives (Keller *et al.*, 2010); adding DMC to the electrolyte in a lithium ion battery significantly increases the conductivity as well as decreases the viscosity and resistance of electrolyte, thus improves the efficiency of electrochemical cycles (Berhil *et al.*, 1995; Naejus *et al.*, 1998).

Several industrialized processes for DMC synthesis have been developed by companies in Germany, France, Italy, U.S., Canada, etc., since 1980s, based on the reactions including (1) phosgenation (phosgene process), (2) the liquid phase methanol oxycarbonylation (the Enichem process), (3) the methylnitrite carbonylation (the UBE process), (4) the vapour phase methanol oxycarbonylation, and (5) the transesterification (Keller *et al.*, 2010). The phosgene process is performed following a two-step process through the reaction of methanol on phosgene (Eqs. (6) and (7)); the Enichem process by liquid phase methanol oxycarbonylation (as a contraction of oxidative carbonylation) is based on the catalytic reaction of liquid methanol, carbon monoxide and oxygen via catalysts at a temperature range of 120–140°C and a total pressure range of 2–4 MPa (Eq. (8)); the UBE process by methylnitrite carbonylation is proceeded via the catalytic reaction of methanol, nitrogen monoxide, oxygen and monoxide (Eqs. (9) and (10)). The vapor phase methanol oxycarbonylation, directly derived from the liquid phase Enichem process and based on the same reaction (Eq. (8)), was developed by the Dow Chemical company to overcome the drawbacks in the above processes, which is usually performed at a temperature range of 100–130°C and a total pressure range of 1–3 MPa. The transesterification of both urea and ethylene carbonate (EC, $C_2H_4CO_3$) with methanol (Eqs. (11) and (12)) is another promising process and has been industrialized by companies such as Texaco, Shell, and others in China (Keller *et al.*, 2010).

(a) Phosgenation

$$CH_3OH + COCl_2 \rightarrow ClCOOCH_3 + HCl \quad (6)$$

$$CH_3OH + ClCOOCH_3 \rightarrow (CH_3O)_2CO + HCl \quad (7)$$

(b) Methanol oxycarbonylation

$$2CH_3OH + CO + 1/2O_2 \rightarrow (CH_3O)_2CO + H_2O \quad (8)$$

(c) Methylnitrite carbonylation

$$2CH_3OH + 2NO + 1/2O_2 \rightarrow 2CH_3ONO + H_2O \quad (9)$$

$$2CH_3ONO + CO \xrightarrow{PdCl_2} (CH_3O)_2CO + 2NO \quad (10)$$

(d) Transesterification

$$(NH_2)_2CO + 2CH_3OH \leftrightarrow (CH_3O)_2CO + 2NH_3 \quad (11)$$

$$C_2H_4CO_3 + 2CH_3OH \leftrightarrow (CH_3O)_2CO + HOC_2H_4OH \quad (12)$$

The direct synthesis of DMC from CO_2 is usually attractive and promising due to the conversion of CO_2 into valuable chemicals or energy products is considered as a green way with many advantages. The reaction between methanol and CO_2 to directly produce DMC shown as below has been studied since the 1980s (Hoffman, 1982).

$$2CH_3OH + CO_2 \leftrightarrow (CH_3O)_2CO + H_2O$$
$$\Delta H^0_{298} = -28\ kJ/mol \quad (13)$$

Razali *et al.* (2012) reviewed the direct synthesis of DMC from CO_2 and methanol in view of catalysts, additives, supports, semiconductors and operating conditions. For catalyst, single oxides, bimetallic materials, multicomponent composites, basic compounds are discussed. Carbonaceous and silica materials as supports are addressed in terms of crystalline structure, pore structure, surface chemistry, dispersion of active metal particles and adsorption between reactants and active sites. Several additives like phosphoric acid acted as Brönsted-Lowry acid and alkylating agents for water removal are mentioned. Operating conditions including reaction temperature and CO_2 pressure are discussed as well by Razali *et al.* (2012).

DME

DME is one of the derivatives of methanol that originally derived through distillation of byproducts produced under high-pressure methanol synthesis. The global demand of DME is about 6.3 million tons a year and it generates an annual value around US$ 3.2 billion. It is an easily liquefiable (boiling point of –25°C), thermally-stable, non-toxic, biodegradable and environmentally benign compound, possessing high cetane number and physico-chemical properties similar to liquefied petroleum gas (LPG). Moreover, DME exhibits excellent combustion performance of no sulphur and less NO_x, smoke and hydrocarbons emission compared with LPG and conventional diesel fuel. As a result, DME is considered as an ideal alternative to LPG and diesel fuel in the gas turbines and fuel cell. Furthermore, DME can also be used as LPG blend stock in cooking and heating, as fuels for power generation in combined cycle plants, and as a chemical intermediate for novel pathway to high-value oxygenated compounds (Fleisch *et al.*, 2012; Mbuyi *et al.*, 2012).

The production of DME is an available, well-known and relatively simple process, which is typically composed of the main reactions as methanol formation (Eqs. (1)–(2)), water-gas shift (Eq. (14)) and methanol dehydration (Eq. (15)).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -42 \text{ kJ/mol} \quad (14)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^0_{298} = -23 \text{ kJ/mol} \quad (15)$$

Several companies have developed two-step and direct DME synthesis technologies, which are also the main licensors for methanol production. Similar to the methanol formation, CO or CO_2 as carbon source, hydrogen source and catalyst to activate carbon source are required to produce DME. In this two-step synthesis, the methanol synthesis and water-gas shift reactions are described in the above section. Methanol dehydration reaction can be carried out generally using an acidic catalyst like a zeolite or γ-Al_2O_3. In view of thermodynamics, DME synthesis is an exothermic reaction, thus operating at lower temperatures is suggested to avoid the deactivation of the catalyst. In fact, it is a gas-phase reaction typically conducted at a pressure range of 1–2 MPa and a temperature range of 220–250°C due to the activation of CO_2. An attractive route is to directly produce DME in a single reactor. The direct DME synthesis is considered to break the equilibrium barrier and results in a synergistic effect because the generation of water drives WGS reaction to produce more H_2 which in turns drives the methanol production to produce more methanol. However, the Cu-based catalyst used for methanol production suffer serious deactivation in the presence of water, thus a reformulation for methanol synthesis is generally required. Besides, a series of researches focus on the substitution for Cu in order to release the water-induced deactivation of catalyst (Mbuyi *et al.*, 2012).

The commercialization of a new fuel is usually a big challenge due to competitions from not only conventional fossil fuels with established distribution and marketing infrastructures but also other alternative fuels. Therefore, numerous efforts are currently underway to commercialize DME as an ideal alternative to diesel. Nowadays the market of DME is limited and nearly all of the commercial DME plants for fuel application are built in China. The market of biomass-derived DME is recently attractive and considerable, which exhibits much potential to replace fossil fuel since biomass resources is abundant and renewable. In general, DME is considered to be able to overcome this challenge mainly due to a relatively simple technology of DME production from methanol, in which methanol market has been established and gradually grows up. The applications of DME as fuel are favorable, especially LPG/DME blends as fuels, thus can enhance the opportunities for its introduction and enlarge the market potential. Moreover, a strong supporting and driving force from a Canadian company, Methanex, which is also the global leader in methanol market and has proposed several DME-related projects, is another key to achieve the commercialization of DME production.

HYDROGEN SOURCE

Since CO_2 is just a source of carbon without hydrogen, a clean, sustainable and cheap source of hydrogen should be developed for CO_2 utilization to chemicals or energy products. Hydrogen is conventionally produced from fossil fuels, roughly 96% by steam reforming (SR) of natural gas. Other relatively widespread processes to produce syngas from hydrocarbon fuels are partial oxidation (POX) and autothermal reforming (ATR). These techniques generally produce a great deal of CO (Table 3). Additional reactors for water-gas shift (WGS) reaction are generally used. From both economic and practical aspects, coal instead of other hydrocarbon fuels is gasified via POX method with steam and oxygen at high temperature and pressure, which is called the integrated gasification combined cycle (IGCC) technology as well as clean coal technology. These conventional technologies coupled with CCS may be acceptable to reduce the CO_2 emission; however, the use of fossil fuels is not renewable and several drawbacks restrict the progress such as the coal gasification technique is very expensive, complex, perhaps dangerous, and involves so-far unsolved problems (Armaroli and Balzani, 2011a).

A variety of researches have focused on the development of novel technologies for reliable and cost-effective H_2 production from coal, other fossil fuels or biomass. The chemical looping process (CLP), as one of the promising technologies to produce H_2 with in situ CO_2 capture, has been proposed and successfully implemented in pilot scale plants. Two key applications for CLPs, chemical looping combustion (CLC) and chemical looping gasification (CLG) are described. A CLC process uses carbonaceous fuel sources as feed to reduce the metal oxide oxygen carriers and to generate heat for electricity by oxidizing the reduced metal oxide oxygen carrier with air. Alternatively, a CLG process utilizes steam and/or CO_2 to partially oxidize the reduced oxygen carrier to produce H_2 and/or CO, which can be further processed to generate liquid fuels, chemicals, and/or electricity via conventional techniques. Under these reduction-oxidation reaction cycles, carbonaceous fuels could then be converted to highly concentrated streams of H_2 and CO_2 and high-quality heat (Zeng *et al.*, 2012; Tong *et al.*, 2013).

In addition, a number of potential pathways to produce clean hydrogen are proposed as well, such as biomass decomposition or water splitting by thermolysis, solar energy and biological process. Among them, water electrolysis is believed to be a potentially promising method to produce clean hydrogen since electricity can be supplied from renewable energy. Moreover, biomass decomposition is also a potential route to supply hydrogen under a net CO_2 reduction condition (Abbasi and Abbasi, 2011; Armaroli and Balzani, 2011a; Bičáková and Straka, 2012; Ngoh and Njomo, 2012; Pearson *et al.*, 2012; Li *et al.*, 2013).

Thermolysis

Thermolysis, or thermal decomposition, is a series of chemical reactions initiated by heat or energy input. Thermolysis of biomass or hydrocarbons is operated in the

Table 3. Conventional hydrogen production processes from fossil fuels.

Methodology	Reaction		Catalyst	η (%)	Specification
Steam reforming (SR)	$CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2$ $CH_4 + 2H_2O_{(g)} \rightarrow CO_2 + 4H_2$	(Endothermic) (Endothermic)	Ni-based	70–85	• Provide over 90% H_2 production • Low operational and production cost • The higher H/C, the lower CO_2 production • 7.05 kg CO_2 emission per 1 kg H_2 production • Steam (500–900°C, 0.3–2.5 MPa)
Partial oxidation (POX)	$CH_4 + O_2 \rightarrow CO + 2H_2$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2$	(Exothermic) (Exothermic) (Endothermic)	Ni Rh	60–75	• No water demand, only O_2 • Low operational cost • Smaller size, simple system
Autothermal reforming (ATR)	$3CH_4 + H_2O_{(g)} + O_2 \rightarrow 3CO + 7H_2$	(Exothermic)			• High conversion cost • Steam (700–1500°C, 3–8 MPa)
Water-gas shift (WGS)	$CO + H_2O_{(g)} \rightarrow CO_2 + H_2$ $CO_2 + H_2 \rightarrow CO + H_2O$	(Exothermic) (Endothermic)	Cr_2O_3 Fe_2O_3 Fe-Pd alloy Co/ZnO Rh, Ru, Pt, Cu	-	• Purification method: pressure-swing adsorption, cryogenic distillation, membrane • Steam (400–500°C) • Separation: stage 1: 350–370°C, stage 2: 200–220°C

range of approximately 200–3,000°C. Such thermochemical processes can be classified as oxidation (combustion) and reduction processes (reforming, pyrolysis and gasification) according to the character of the chemical reaction, in which hydrogen is generally produced via the reduction processes (Bičáková and Straka, 2012). Steam reforming of natural gas or methane contributes 96% worldwide production of hydrogen as described above. Hydrocarbons react with water vapor to form syngas, a gas mixture of CO and hydrogen, in the presence of nickel as catalyst under very high temperatures around 840–950°C and moderate pressures around 2–3 MPa. Pyrolysis, also called cracking or dry distillation, is to decompose hydrocarbons thermochemically at elevated temperature in the absences of oxygen (or any halogen) to produce hydrogen and char. A typical pyrolysis process is the cracking of methane proposed by Matovitch and further progresses by Steinberg (Steinberg, 1986; Ngoh and Njomo, 2012). This reaction is theoretically complete within around 1600°C and is presented below:

$$CH_4 \rightarrow C_{(s)} + 2H_2 \quad \Delta H = 75 \text{ kJ/mol (endothermic)} \quad (16)$$

Gasification, developed in the 1800s, was previously used to produce gas for light and heat from organic materials. Gasification is the process to convert hydrocarbons into syngas. Feedstock, e.g., biomass, organic wastes or coal, can be cleaned via gasification by reducing the impurities like potassium and chloride. Therefore, syngas burns cleanly without harmful emissions. Gasification is also considered as a highly efficient method to generate energy from organic materials. In addition, energy is more extracted in syngas than in organic materials. Currently, four types of commercial gasifier are available, i.e., counter current fixed bed, co-current fixed bed, fluidized bed and entrained flow bed. Several parameters need to be concerned, such as the temperature, pressure and type of gas (air, vapor, O_2, etc.) used in gasification (Shimura and Yoshida, 2011; Ngoh and Njomo, 2012).

Thermochemical water-splitting cycles have been developed since the 1970s and are generally coupled with nuclear or solar energy system for hydrogen production. Nowadays the total efficiency for these thermochemical cycles is around 50%. However, theoretically an extremely high temperature over 2,500°C is required (Orhan *et al.*, 2012). Therefore chemical reagents are generally used to lower down the reaction temperature of thermolysis in those thermochemical cycles which are tabularized in Table 4 (Lewis and Masin, 2009; Bičáková and Straka, 2012; Orhan *et al.*, 2012). Moreover, thermodynamic study is essential for these thermochemical cycles to economically improve the efficiency and scale up the process. The limiting thermodynamic efficiencies of thermochemical cycles for hydrogen production have been extensively investigated by Ewan and Allen (2006), who provided a useful basis for the comparison between cycles and the identification of strengths and weaknesses within cycles. In general, more steps result in lower operating temperature and lower the efficiency. Moreover, more materials, heat and corrosive chemicals must be managed and controlled.

Table 4. Hydrogen production by thermolysis of water.

Type	Reaction	Temperature (°C)	η (%)
Sulfur-Iodine cycle	$2I_2 + 2SO_2 + 4H_2O \rightarrow 4HI + 2H_2SO_4$	20–100	40–50
	$4HI \rightarrow 2I_2 + 2H_2$	300–500	
	$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2$	400–800	
Sulfur-ammonia cycle	$2SO_2 + 4NH_3 + 2H_2O \rightarrow 2(NH_2)_2SO_3$	25	26–50
	$2(NH_2)_2SO_3 + 2H_2O \rightarrow 2(NH_2)_2SO_4 + 2H_2$	80	
	$2(NH_2)_2SO_4 \rightarrow 4NH_3 + 2H_2SO_4$	350	
	$2H_2SO_4 \rightarrow 2SO_3 + 2H_2O$	400	
	$2SO_3 \rightarrow 2SO_2 + O_2$	850	
Kapra Mark–10	$2I_2 + 2SO_2 + 4H_2O + 8NH_3 \rightarrow 4NH_4I + 2(NH_4)_2SO_4$	50	-
	$2(NH_4)_2SO_4 + 2Na_2SO_4 \rightarrow 2Na_2S_2O_7 + 4NH_3 + 2H_2O$	400	
	$2Na_2S_2O_7 \rightarrow 2SO_3 + 2Na_2SO_4$	550	
	$2SO_3 \rightarrow 2SO_2 + O_2$	870	
	$4NH_4I \rightarrow 4NH_3 + 2I_2 + 2H_2$	630	
Ca–Br cycle	$2CaBr_2 + 2H_2O \rightarrow 4HBr + 2CaO$	770	40–50
	$4HBr \rightarrow 2Br_2 + 2H_2$	80	
	$2CaO + 2Br_2 \rightarrow 2CaBr_2 + O_2$	550	
UT-3 cycle	$2CaBr_2 + 2H_2O \rightarrow 4HBr + 2CaO$	730	40–50
	$2Fe_3O_4 + 16HBr \rightarrow 6FeBr_2 + 8H_2O + 2Br_2$	300	
	$6FeBr_2 + 8H_2O \rightarrow 2Fe_3O_4 + 12HBr + 2H_2$	540	
	$2CaO + 2Br_2 \rightarrow 2CaBr_2 + O_2$	430	
Fe–Cl cycle	$6FeCl_2 + 8H_2O \rightarrow 2Fe_3O_4 + 12HCl + 2H_2$	925	49
	$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$	925	
	$2Fe_3O_4 + 16HCl \rightarrow 2FeCl_2 + 4FeCl_3 + 8H_2O$	125	
	$4FeCl_3 \rightarrow 4FeCl_2 + 2Cl_2$	425	
Cu–Cl cycle	$4CuCl_2 + 2H_2O \rightarrow 2Cu_2OCl_2 + 4HCl$	425	27
	$4HCl + 4Cu \rightarrow 4CuCl + 2H_2$	425	
	$2Cu_2OCl_2 \rightarrow 4CuCl + O_2$	525	
	$8CuCl \rightarrow 4CuCl_2 + 4Cu$	25	
Cu–SO_4 cycle	$2CuO + 2SO_2 + 2H_2O \rightarrow 2CuSO_4 + 2H_2$	25	25
	$2CuSO_4 \rightarrow 2CuO + 2SO_2 + O_2$	825	
	$2CuO + 2SO_2 + xH_2O \rightarrow 2CuSO_4\cdot(x - 1)H_2O$	25	
	$2CuSO_4\cdot(x - 1)H_2O \rightarrow CuSO_4 + 4H_2O$	525	
V–Cl cycle	$4VCl_2 + 4HCl + 4nH_2O \rightarrow 4(VCl_3\cdot nH_2O) + 2H_2$	120	31–46
	$4(VCl_3\cdot nH_2O) \rightarrow 4VCl_3 + 4nH_2O$	160	
	$8VCl_3 \rightarrow 4VCl_4 + 4VCl_2$	766	
	$4VCl_4 \rightarrow 4VCl_3 + Cl_2$	200	
	$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$	875	
Ce–Cl cycle	$4CeO_2 + 16HCl \rightarrow 4CeCl_3 + 2Cl_2 + 8H_2O$	110	21
	$4CeCl_3 + 8H_2O \rightarrow 4CeO_2 + 12HCl + 2H_2$	925	
	$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$	850	

Thermolysis process faces several challenges such as low rates of conversion, gas separation, corrosion of materials to equipment at high temperature and high pressure, energy losses across multiple steps during heat exchange, undesired side reactions, etc. Moreover, these processes are still uncompetitive with the other technologies of hydrogen production in terms of efficiency and cost (Funk, 2001; Abbasi and Abbasi, 2011; Graves *et al.*, 2011; Bičáková and Straka, 2012).

Solar Energy Process

Solar hydrogen, namely hydrogen produced via solar energy, is considered as a promising solution to energy and environmental problems. Typically, solar hydrogen can be produced by solar thermal system and direct photoconversion, which is shown in Table 5. The solar thermal system, namely photolysis, is similar to the thermolysis process as described above, which is operated at a temperature ranging of 200–2,000°C with a maximum efficiency up to 70%. Theoretically, solar radiation is concentrated to heat up water to its dissociation temperature and results in hydrogen and oxygen by water splitting. Such concentrated solar power possesses several advantages, such as no fossil fuel needed, no generation of pollution, and viability of set-up in desert areas. However, the intermittent nature of solar energy as heat source is the severe limitation on the whole system. The thermal energy transfer throughout the system in a narrow temperature range also restrains the

Table 5. Solar hydrogen processes.

Methodology	Reaction	Catalyst	η (%)	Specification
Photolysis	$2H_2O + \text{light} \rightarrow 2H_2 + O_2$		< 70	• H_2 directly produced from water and light • Operating temperature: 200–2000°C
Direct biophotolysis	$2H_2O + \text{microalgae} + \text{light} \rightarrow 2H_2 + O_2$	Algae Chlamydomonas reinhardtii Anabaena sp. Enzyme	< 15	• H_2 directly produced from water and light • High intensity of light required • Recombination process • Low photochemical efficiency
Indirect biophotolysis	$6H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$ $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$ $12H_2O + \text{light} \rightarrow 6O_2 + 12H_2$ (overall)	Microorganism Green algae Cyanobacteria	< 0.5	• N_2 can be fixed from atmosphere • Hydrogenase enzymes should be controlled • 30% O_2 present and inhibits H_2 production
Photofermentation	$CH_3COOH + 2H_2O + \text{light} \rightarrow 2CO_2 + 4H_2$	Hydrogenase Nitrogenase	< 0.1	• Operating at mild condition • Slow kinetic, high energy demand • High capital cost
Photoelectrochemical (PEC)	$2H_2O + \text{light} \rightarrow 2H_2 + O_2$	Semiconductor	< 15	• Low current density (0.03 A/cm^2) • Recombination of H_2 and O_2

efficiency. As a result, no viable process for hydrogen production by solar thermal system is commercialized so far (Abbasi and Abbasi, 2011; Armaroli and Balzani, 2011a; Ngoh and Njomo, 2012).

Solar hydrogen via direct photoconversion (e.g., photocatalytic, photoelectrochemical, and photobiological processes) is nowadays well-developed and exhibits several advantages over solar thermal system such as simplicity and operation at mild conditions (Abbasi and Abbasi, 2011). Photocatalytic systems are applied to which biomass and water can be converted to hydrogen by solar energy and photocatalyst. A variety of methods have been carried out to improve the photocatalytic efficiency, e.g., the use of sensitizer like dyes for visible light absorption, the development and modification of various photocatalysts and cocatalysts, the morphology control of photocatalysts and optimization of reaction conditions (Shimura and Yoshida, 2011).

Photoelectrochemical (PEC) processes are typically the use of semiconductors as photoactive electrodes illuminated by sunlight to decompose water into hydrogen and oxygen. The key to successful development of photoelectrochemical process rely on the photoelectrode materials and their interface properties. In principle, a limited band gap of electrodes is necessary for photoelectron effectively excited from solar spectrum (< 2.2 eV) and for excited photoelectron with enough energy to split water (> 1.23 eV). Moreover, the band edges must stride across the redox potentials of water electrolysis. As a result, researches have been made to promote the performance of photoelectrode materials, mainly based on visible light absorption as well as the efficiency, separation and transport of photo-induced charges. Several strategies have been developed such as (1) the doping of elements to tune the band gap of semiconductors, i.e., a broader band gap to enhance visible light absorption and a narrow band gap to promote charge transport; (2) the surface treatment to remove or diminish the recombination phenomena; (3) the selection of electrocatalyst to decrease the overpotentials; (4) the morphology control to enhance visible light absorption and shorten the transport of the photo-induced charges; (5) the application of sensitizer, passivating layer, heterojunction structure, etc., to improve the photoelectrochemical efficiency (Graves *et al.*, 2011; Li *et al.*, 2013).

Photobiological processes produce hydrogen from water via biological processes coupled with solar energy, organisms (e.g., green algae, cyanobacteria and photosynthetic bacteria) and enzymes (e.g., hydrogenase and nitrogenase). Hydrogenases exist in most of the photosynthetic organisms and can be classified into uptake hydrogenases and reversible hydrogenases, which have the ability to consume and create molecular hydrogen, respectively. The photobiological process can be classified as direct biophotolysis, indirect biophotolysis and photofermentation. Direct biophotolysis, generally for water splitting, utilizes the photosynthetic system via organisms to transform solar energy into the chemical energy (Eq. (17)). They are much potential because of several advantages, such as abundant sources (water and sunlight), low cost biological catalysts, ambient operating condition and less energy required operation as compared with present industrial processes (Bičáková and Straka, 2012; Ngoh and Njomo, 2012).

$$2H_2O + \text{microalgae} \xrightarrow{\text{solar light}} 2H_2 + O_2 \tag{17}$$

Indirect biophotolysis includes four steps: the biomass production via photosynthesis, the concentration of biomass, aerobic dark fermentation, and the conversion of acetate (Eqs. (18)–(19)). Hydrogen can also be produced under anaerobic condition, in which nitrogen can be fixed from atmosphere as well (Eq. (18)). However, both direct and indirect biophotolysis processes face several challenges for large scale production such as the recombination process, the degradation of produced hydrogen by uptake hydrogenase, the diffusion of solar energy and the consequent low energy density thus leading to low rate and low yield of hydrogen production, and so on (Bičáková and Straka, 2012; Ngoh and Njomo, 2012).

$$6H_2O + 6CO_2 \xrightarrow{\text{solar light}} C_6H_{12}O_6 + 6O_2 \tag{18}$$

$$C_6H_{12}O_6 + 6H_2O \xrightarrow{\text{solar light}} 6CO_2 + 12H_2 \tag{19}$$

Photofermentation is generally used to decompose organic materials or biomass into hydrogen and CO_2 via photosynthetic bacteria with solar energy. This process can be carried out under anaerobic conditions and the optimal condition is mild at 30–35°C and neutral pH (Eq. (20)). The advantage of this process is that a wide spectral light energy can be used by selected bacteria and various organic wastes can be feedstock. However, several disadvantages need to be overcome such as the slow hydrogen production rate, an inhibitory effect on nitrogenase by oxygen, low conversion efficiency of solar light (only 1–5%), and the requirement of large reactor surface, i.e., high capital cost (Bičáková and Straka, 2012; Ngoh and Njomo, 2012).

$$CH_3COOH + 2H_2O \xrightarrow{\text{solar light}} 2CO_2 + 4H_2 \tag{20}$$

Water Electrolysis

Water electrolysis provides approximately 4% of hydrogen worldwide and could be a promising, ecological and friendly process in the future only if the electricity is from renewable energy sources. This well-known process has been commercialized since 1890, in which fundamentally a direct current passes through two electrodes in a water solution, resulting in the break of chemical bonds of water into hydrogen and oxygen. Simplicity in operation and easy separation of products are the attractive parts for this technique. No greenhouse is generated during the electrolysis process and both hydrogen and oxygen produced can be further industrially applied. Basically, about 9 ton of water and 50 MWh of electricity are consumed to produce one ton of hydrogen accompanied with 8 ton of oxygen (Armaroli and Balzani, 2011a). The energy efficiency, defined as a ratio of chemical energy acquired to electrical energy supplied, is reported to reach 50–70% in practical use (Bičáková and Straka, 2012). Although theoretically operation at near 100% efficiency is possible, the efficiency is actually sacrificed to increase the current density. As a result, a sufficiently clean and economic source of power generation should be concerned to make this technology practical. Moreover, the capital cost and the operating cost should be optimized in view of economics. The former depends on the operating current density and operating times, while the later depends on the energy efficiency related to the operating voltage.

The electrolysis technologies can be generally classified into two types: low-temperature electrolysis (LTE) and high-temperature electrolysis (HTE), which are shown in Table 6. Alkaline water electrolysis (AWE) cells, the dominant type of LTE cells, have been developed since 1960s and are commercially available nowadays. Typically, an electrolyte of 30 wt% KOH solution, the electrodes of porous Raney nickel alloy, and an operating temperature at 70–100°C are applied in AWE cells. The easily replaced components and high durability make the AWE cells more potential and economic. Advanced AWE cells, now at a demonstrated stage, are designed to operate at higher temperature and/or high pressure so that high current density and high pressure hydrogen production are obtained. Seawater electrolysis, conventionally used to produce chlorine gas, is also considered as a modified AWE since it is naturally alkaline. However, the anode materials must be specifically selected (e.g., Mo- and W-doped MnO_2) to exhibit a potential range below the chlorine potential and above the oxygen potential in order to avoid the generation of toxic chlorine gas (Graves *et al.*, 2011; Bičáková and Straka, 2012). Proton exchange membrane (PEM) cells, another type of LTE cells, are typically a polymer electrolyte membrane (thin Nafion polymer) as gas separator to conduct protons in which black platinum, iridium, ruthenium and rhodium are used as electrode catalysts. PEM cells are more efficient than AWE ones; however, their capital cost is higher than that of AWE ones because of the expensive noble metal electrode catalysts and expensive membranes. As a result, high current density up to 1 A/cm^2 is usually operated in order to offset the high cost of PEM cells materials, although such high current density is still not enough to make up for the cost at present (Graves *et al.*, 2011; Bičáková and Straka, 2012).

High-temperature electrolysis (HTE) techniques, typically operated over 500°C, possess both advantages of thermodynamics and reaction rates. Such high temperature operation with fast reaction kinetics can release the dependence on expensive catalyst materials. Solid oxide electrolysis (SOE) cells, the dominant type of HTE cells, have been developed since 1975, which use a solid material as an electrolyte and work like the AWE cells. Because of operating at high temperature, the long-term durability of electrode material is highly concerned recently. Typically, porous metal ceramic composites are used as electrode, e.g., Ni-YSZ for cathode and LSMO with YSZ for anode, and an operating temperature range of 500–800°C is applied in SOE cells (YSZ, yttria-stabilized zirconia; LSMO, lanthanum strontium manganite). SOE cells can be used for not only steam electrolysis, but also CO_2 electrolysis and co-electrolysis of both water and CO_2. Moreover, syngas can be directly produced via co-electrolysis of water and CO_2 in SOE cells without additional RWGS reactors. They also provide economic advantage in capital cost and operating cost and an additional profit from the production of syngas. However, several challenges need to be overcome such as more complicated heat management, easily energy losses and underestimated cost due to failures of materials or equipment and demand of additional system. Direct molten carbonate electrolysis (MCE), another type of HTE techniques, conducts carbonate ions in anode and electrolyze CO_2 to CO as well as H_2O to H_2. However, only few works report the development of MCE cells. Additional energy is required to separate CO_2 from O_2 to avoid the release of CO_2. In addition, the low current density (< 0.1 A/cm), the uncertain long-term durability, the performance of MCE cells that has not been optimized, and the corrosive molten carbonate are the challenges that need to overcome (Graves *et al.*, 2011; Bičáková and Straka, 2012).

In general, low temperature operation advantageously sustains microstructure and nanoparticles of cells (related to fast kinetics) against sintering and agglomeration (related to high performance), while it disadvantageously increases demands of thermodynamic energy and electrical energy per unit fuel produced (related to slow kinetics). Therefore, the cell performance is potentially balanced. On the contrary, high temperature operation leads to high production rate of hydrogen; however, the degradation in performance via sintering and agglomeration is also observed.

Renewable Energy Source

Although water electrolysis is a promising technique, a sufficiently large power capacity using renewable energy should be concerned besides electrolyzer. The renewable energy resources including water, wind, sun, biomass, and heat from the earth (namely geothermal) are proposed as alternatives since they can generate secure, reliable and affordable energy with reduced price volatility. Christopher and Dimitrios (2012) reviewed hydrogen production from renewable energy sources concerned with exergy. They demonstrated that renewable energy resources are free so the exergy efficiency has an impact on the cost of the construction of the processes, exhibiting much potential on the development of renewable energy. At the end of 2012, renewable energy capacity exceeded 1,470 GW, up about 8.5% from 2011, providing an estimated 21.7% of the world's electricity (IRENA, 2013; REN21, 2013).

Hydropower, based on the natural water cycle, is the most mature, reliable and cost-effective renewable power generation technology. The design of hydropower is flexible to fit a variety of demands in capacity factor. Hydropower is also the largest source of renewable power generation worldwide with an installed capacity around 990 GW in 2012, up about 3.1% from 2011. An estimated 3,700 TWh of electricity is generated via hydropower in 2012, providing 16.5% of global electricity. Today over 11,000 hydropower plants in 150 countries are established to generate electricity. The world leaders in hydropower are China (228 GW, 864

Table 6. Hydrogen production by electrolysis of water.

Type	Reaction	η (%)	Temp. (°C)	ID (-A/cm^2)	Specification
Alkaline water electrolyzer (AWE)	(Cathod) $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ (Anode) $2OH^-_{(aq)} \rightarrow 2e^- + 1/2O_{2(g)} + H_2O_{(l)}$	50–60	70–100	0.01–0.02	• Easy replacement • High durability (10–20 years)
Proton Exchange Membrane (PEM)	(Cathod) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ (Anode) $H_2O(l) \rightarrow 2H^+_{(aq)} + 2e^- + 1/2O_2$	55–70	80–100	1	• High capital cost • High current density
Solid oxide electrolyzer (SOE)	(Cathod) $H_2O_{(g)} + 2e^- \rightarrow H_{2(g)} + O^{2-}$ (Anode) $O^{2-} \rightarrow 2e^- + 1/2O_{2(g)}$	40–60	500–950	0.16–3.6	• High current density • Effective heat utilization • Less usage of electrical energy
Molten carbonate electrolyzer (MCE)	(Cathod) $H_2O_{(l)} + CO_{2(g)} + 2e^- \rightarrow H_{2(g)} + CO_3^{2-}$ $2CO_{2(g)} + 2e^- \rightarrow CO + CO_3^{2-}$ (Anode) $CO_3^{2-} \rightarrow 2e^- + 1/2O_{2(g)} + CO_{2(g)}$	40–50	600–750	< 0.1	• Low current density • Inexpensive electrode materials • Molten carbonate is corrosive

TWh), Brazil (84GW, 441 TWh), Canada (77GW, 376 TWh), and the United States (78GW, 277 TWh). The outlook for the growth in hydropower capacity are more likely to be slow and steady than rapid, due to the project design, process design, and financial issues. In addition, the conventional hydropower activities focus on the addition of new generating capacity, the improvement of efficiency or capacity at existing hydroelectric facilities, the addition of hydroelectric generating capacity to existing non-powered dams and the increase of advanced pumped-storage hydropower capacity. In general, hydropower is the only economically viable large-scale generation technology available today despite other promising energy generation technologies under development. It is a relatively efficient energy storage option as well (IRENA, 2012c; REN21, 2013).

Wind, an abundant, clean, but intermittent energy source, is the fastest growing technology in the world with a significant potential evaluated to be about 75 TW (Armaroli and Balzani, 2011a, b). The global installed wind capacity was about 283 GW at the end of 2012, up about 19% from 2011 (GWEC, 2012; REN21, 2013). The United States and China, the leading countries in wind power, together accounted for nearly 60% of the global market in 2012, followed distantly by Germany, India, and the United Kingdom. Wind power is typically the use of wind turbines to make electricity, wind mills for mechanical power, wind pumps for pumping water or drainage, or sails to propel ships. Wind power technologies vary in sizes and styles and can generally be classified according to the axis direction of wind turbines (horizontal or vertical) and the location (onshore or offshore). The power generation of wind turbines is determined by the capacity of the turbine (in kW or MW), the wind speed, the height of turbine and the diameter of rotors. The current average size of grid-connected wind turbines is around 1.16 MW, while most new projects use wind turbines between 2 MW and 3 MW. Offshore wind turbines show advantages of high average mean wind speeds and the ability to build very large turbines with large rotor diameters, although this trend is not confined to offshore. Larger turbines provide greater efficiency and economy, but they are also more complex to build, transport and deploy. For economical aspect, wind power has even been competitive with power from fossil fuels in some areas. However, the main challenges are the intermittence of wind energy resulting in a capacity factor of about 30% and the corrosion problems for turbines exposed to air pollution, UV radiation as well as salts especially for offshore cases (IRENA, 2012e; REN21, 2013).

Solar energy, another abundant, clean but intermittent energy source as well, can be directly and indirectly converted to electricity from the sun via several techniques. Only concentrated solar power (CSP) and solar photovoltaic (PV) cell are practical to provide significant amount of electricity. A CSP system generates electricity by the use of heat converted from the concentration of sunlight in a large area. The global installed CSP capacity had increased to around 2.5 GW in 2012, up about 0.56% from 2011. There are currently dozens of CSP plants under construction, and more than 20 GW under development worldwide. Spain and the United States are the two leading CSP markets driven by their government support schemes, and both of them together contain 90% of the current installed CSP capacity. There are four main types of CSP technologies such as Parabolic and Fresnel through, solar tower and Parabolic dish, Among them, Parabolic trough plant is the most widely and commercially deployed CSP plant, although it is not a mature technology and improvements in performance and cost reductions are required. Solar tower may become the technology of choice in the future, because very high temperatures are achievable to increase the steam cycle efficiency and reduce the cost of thermal energy storage by allowing a higher temperature differential (IRENA, 2012b; REN21, 2013). In general, CSP plants can couple with a thermal storage system to reduce the impact from the intermittent sunlight, thus can increase the CSP capacity factor compared with solar cell system and make them more economically competitive. Moreover, the advances in solar concentrator and thermal storage system can benefit CSP technologies as well.

Solar PV technologies based on the PEC process are typically an electrolysis cell powered by solar energy and currently a well-established technology. The global installed solar PV capacity had increased to around 100 GW in 2012, up about 41% from 2011. Germany, Italy, China, the United States, and Japan are the leaders for market and total capacity of PV cells. PV technologies can be classified into three generations according to materials and the level of commercial maturity. First-generation PV system, fully commercialized, uses the wafer-based (single/multiple) crystalline silicon technologies. Second-generation PV system, early market deployed, is mainly based on thin-film PV technologies and generally classified as two types: silicon (amorphous and micromorph) and metal composites. Third-generation PV system, at the pre-commercial stage, is mainly focus on concentrating PV, dye-sensitized solar cells (DSSC), organic solar cells and novel and emerging solar cell concepts (IRENA, 2012d; REN21, 2013). However, the high cost and low energy efficiency are still the main challenges in solar PV technologies. To improve the energy efficiency of solar PV to generate hydrogen, several techniques have been developed, e.g., the promotion of solar modules and electrolyzer. The integration of heat between solar cell and electrolyzer is also a possible strategy to improve the energy efficiency, because high temperature deteriorates the efficiency of solar cell system but benefits to the efficiency of electrolyzer (Abbasi and Abbasi, 2011; Armaroli and Balzani, 2011a).

Biomass, a large variety of organic materials generated by sunlight and CO_2, is one of the most prospective renewable resources. The use of biomass in the heat, power and transport sectors increases to around 55 EJ. The global installed biomass heat capacity was around 293 GW, while bio-power capacity was up to 83 GW in 2012. Generally, three critical factors should be considered for power generation by biomass including (1) biomass feedstock, (2) biomass conversion and (3) power generation technology. Both the production of biomass feedstock and its conversion to useful energy usually vary with environments, regions, social and economic aspects, etc. As a result, secure, long-term supplies of low-cost, sustainable sourced feedstock as well as its transportation to destination should be taken into account for economical biomass power plants. When biomass is collected, this feedstock is transformed into energy via biomass conversion including thermo-chemical processes (i.e., combustion, gasification, and pyrolysis) or bio-chemical processes like anaerobic digestion and fermentation. The resultant energy would be further used to generate heat and/or electricity (IRENA, 2012a; REN21, 2013).

In general, the intermittence, fluctuation and non-availability of these renewable energy resources all the time throughout the year do exist and restrict the development themselves. The idea of hybrid system of renewable energy resources is generally proposed and has recently studied in the design, optimization, operation and control. However, there are still many challenges in terms of efficiency and optimization that need to be overcome (Bajpai and Dash, 2012).

CONCLUSION

CO_2 mitigation presents both a challenge and an opportunity to the world for sustainability of energy and environment. Global strategies of CO_2 mitigation should focus on the utilization of CO_2, for example, the use of CO_2 for the environmentally benign processes, the production of industrially useful chemicals from CO_2, and the CO_2 recycling combined with renewable energy to conserve carbon sources.

The use of microalgae exhibits a number of advantages over other plant feedstock in CO_2 capture and utilization concerned with (1) high photosynthetic conversion, (2) rapid production, (3) high capacity to produce a wide variety of biofuel feedstock, (4) high capability of environmental bioremediation such as CO_2 fixation from atmosphere/flue gas and water purification, and (5) non-competitiveness for land with crops and food. The use of microalgae for biological carbon mitigation shows enormous potential as CO_2 can not only directly be utilized in both extraction and transesterification processes but also directly be applied in the cultivation of microalgae. In general, the cultivation of microalgae can extensively utilize CO_2 and the harvested microalgae can be further used to produce energy, food, chemicals and valuable nutrients. In addition, the net CO_2 emission is assumed to be essentially zero if CO_2 released from the biomass-derived energy can be recycled and reused by cultivation of microalgae. As a result, these advantages and potentials make microalgae a suitable candidate to solve CO_2 reduction and energy issues. However, full-scale industrial application of microalgae biotechnology has not been accomplished yet. More research should be addressed mainly on the development of microalgae with increasing lipid content as well as the conversion of microalgae to biofuels with low energy consumption and low CO_2 emission.

The utilization of CO_2 to produce chemicals like urea and cyclic carbonates is promising and can be a solution to reduce CO_2 emission. In view of thermodynamics of CO_2 conversion, the developments of new reaction processes and/or effective catalyst are required to achieve high performance. However, it should be addressed that the amount of the generated chemicals from the utilization of CO_2 is not high enough to consume most of the captured CO_2 and significantly lower CCS costs. Therefore, the conversion of CO_2 to energy products, for example, methanol, DMC and DME, is believed to be an alternative to consume more CO_2 because of a potentially extensive market scale. Moreover, the production of energy products can reduce the dependence of fossil fuels, thus stimulating the market growth of CO_2 utilization as well. However, the cost of sustainable CO_2-cycled energy products is still not competitive to that of conventional energy products from fossil fuels. In addition, all the technologies are still under development, thus there are no available commercial processes yet. To determine the potential of these chemicals, more details on fundamentals, techniques and cost are required in order to make a comprehensive assessment of these chemicals. Moreover, 3E (energy, economics, environments) evaluation is essential in the near future. In general, considering the expected shortage of fossil fuel, the target of negative carbon emission, carbon tax in future and an inevitable cost down of production from advanced technologies, utilization of CO_2 to produce energy products is believed to be potential in the future.

Since CO_2 is just a carbon source without hydrogen, clean, sustainable and cheap sources of hydrogen should be developed for CO_2 utilization to chemicals or energy products. A number of potential pathways to produce clean hydrogen have been proposed including biomass decomposition or water splitting by thermolysis, solar energy and biological process. According to the advantages and disadvantages among these methods, water electrolysis using electricity supplied from renewable energy as well as biomass decomposition are the most promising techniques.

Nowadays a number of barriers still exist and slow down the advancement of these CO_2 utilization technologies, such as: (1) CO_2 utilization is much less supported as compared to many energy-related technologies; (2) fossil fuel plants are still benefited currently by energy regulations; (3) CO_2 utilization technologies that can result in net CO_2 reduction at commercial scale are yet to be demonstrated. Therefore, more research is necessary towards effective CO_2 utilization technologies.

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