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REVIEW

Recent development of integrating CO_2 hydrogenation into methanol with ocean thermal energy conversion (OTEC) as potential source of green energy

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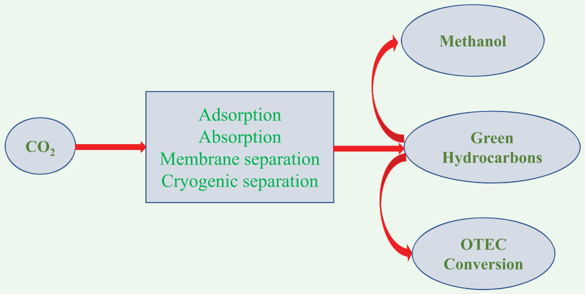
ABSTRACT

Renewable energies have gained momentum in energy transition agenda based on the benefit of lower emissions of carbon and its compounds. Many technologies have been developed at different technology readiness levels addressing climate change impact with reduced emissions of greenhouse gases such as CO_2. Herein the perspective article, we have reviewed CO_2 capture technologies, such as absorption, adsorption, membrane separation, cryogenic separation and separation via hydrate formation, with further focus on the possibility of utilising ocean thermal energy conversion (OTEC) power to generate green hydrogen and produce low carbon fuels. The potential of OTEC generated hydrogen to produce methanol was explored using a simulation exercise utilising a scenario from a real-life offshore gas production facility. By varying the catalysts and reaction conditions, the findings showed encouraging results of CO_2 conversion of ≥50% and product yield of ≥80%. Considering single path reaction with 90%, 95% and 99% of recycling, the highest prediction of methanol production coupled with CO_2 hydrogenation process was 276.59 metric tonnes per day (MTPD). In addition, based on the assumption of 13.5 million standard cubic feet per day (MMSCFD) of CO_2 produced, 204 MW of OTEC power is required to convert approximately 97.82 MTPD of hydrogen for methanol production making it potentially an industrially viable process.



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OTEC; CO_2 conversion and utilization; green hydrocarbon; methanol production

1. Introduction

The CO_2 emission originating from various sources and from anthropogenic activities is one of the major contributors toward climate change. Among the prime sources is that from the combustion of fossil fuels for electricity generation. It was predicted that CO_2 emissions will continue and rapidly increase if no action was done to mitigate the situation. This will lead to a temperature increase beyond the world's livable temperature levels by the end of twenty-first century (1). The impact of climate change includes, rising of sea levels and reduction of agriculture yield. Transition to clean, renewable and carbon neutral energy technologies would mitigate the impact (2–4). It was postulated that to maintain and stabilize the world's CO_2 concentration at 350 ppm level by 2050, generation of 30 ×

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10^7 KW of carbon-neutral power is needed (5). It is crucial to reduce and maintain CO_2 concentrations at low levels and this can be achieved by converting CO_2 into useful products. Many studies have been done on CO_2 utilization as the source for producing value-added chemicals. One of the most promising processes is the hydrogenation of CO_2 with renewable H_2 for direct eco-friendly methanol production and value-added green hydrocarbon. The term green hydrocarbon refers that hydrocarbon obtained from a process, causing low-carbon emission. Moreover, the hydrocarbons also cause lesser emissions of carbon compounds upon their burning when used as a fuel. The rate of hydrogenation and the selectivity of methanol can both be improved using catalysts. Developing high catalytic activity, selectivity, and stability at CO_2 conversion levels suitable for commercial operations is a substantial problem. The catalytic production of methanol from CO_2 normally necessitates high temperatures since CO_2 is a stable molecule.

In addition, effective CO_2 capture technologies are needed to provide sufficient CO_2 for the hydrogenation to produce methanol. Within the value chain of Carbon Capture and Utilization (CCU) program, efficient CO_2 capture process is a substantial step prior to the CO_2 utilization to ensure zero carbon emission goal. Da costa et al. investigated the capturing of carbon dioxide, and it was found that a large CO_2 emission reduction can be achieved in this way (6). Similarly, CO_2 conversion into the hydrocarbons such as methanol and others is also an interesting way to capture and utilize carbon dioxide. In fact, higher conversion of CO_2 and product selectivity can be achieved. The selection of an appropriate capture technology would warrant the feasibility of the overall techno-economic potential of the CO_2 capture and utilization using renewable hydrogen. The efficient and cleanliness of hydrogen as the source of energy can be proven by its capability to produce 2.75 times the energy yield of that hydrocarbon fuels and zero toxic emission where the only product is water vapor (7).

Interestingly, the renewable hydrogen produced from ocean thermal energy conversion (OTEC) is a potential source to produce value-added green hydrocarbons upon reaction with the captured CO_2. The increase in global warming and commitment toward energy security also led to the exploration of renewable energy technologies from various sources such as solar, wind, hydro, biomass and geothermal. Among them, OTEC is one of the promising green technologies that can fulfill global energy demand and reduce global warming due to excessive CO_2 emission. By utilizing a stable temperature difference between warm surface water and cold deep ocean water, a huge potential of thermal energy can be produced from the thermodynamic cycle and support electricity generation. Malaysia has great potential to harness ocean thermal energy via OTEC technology based on its deep water depth of more than 700 m (8,9). By 2050, as the entry to OTEC potential, it is projected that Malaysia could consider growth of its OTEC resources to at least 12,000,0000 W or 12,000,000 KW, i.e. less than 50% of its minimum total potential of 26,000000 KW over its deep waters of 131,000 km^2 at 700 m isobath or deeper up to 2900 m. By 2050, the amount of hydrogen that could be generated would be 2.1 million tons of H_2/year assuming, (12,000,000 kW, 8750 h/year with 50 kWh/kg$H_2 = 2.1$ million tons of H_2/year]. Furthermore, the huge capacity for OTEC potential in Malaysia is comparable to other tropical and subtropical countries like Fiji, Philippines and Nauru Island (10). Of the State of Sabah, Malaysia, there exists number of sites for the deep-water production (DWP) of oil & gas, including Shell @Malikai (565 m), Shell @Gumusut-Kakap (1220 m), Murphy @Kikeh (1300 m), and PETRONAS Carigali @Rotan (1500 m). There also exists the potential of generating power (11), by converting the heat stored in the warm surface water into electrical energy with OTEC Technology by installing OTEC plants with Electrolyzers, gas Compressors, and compressed hydrogen gas storage on a floating platform, the like of the re-used Ultra Large Crude Carrier (ULCC), anchored adjacent to, but not within the 500 m limit in compliance with the safety requirements of, the DWP oil & gas production units. The generated renewable power, being the net of running OTEC plants, would be taken up in the production of green hydrogen by water electrolysis. Thus, for the conversion of the captured 13.5 MMSCFD of CO_2 into green methanol, 204,000 KW of OTEC power capacity would be required to be developed and installed in order generate 97.82 MTPD of hydrogen, as stated herein.

Technically, the power generated from OTEC can be used to split water via electrolysis process and produce renewable hydrogen. This integrated technology was previously studied in 2002 by researchers from the Japanese International Clean Energy Network Using Hydrogen Conversion (WE-NET) (12). In extension to previous work, Kazim et al. (13) investigated the effect of temperature gradient on hydrogen production from OTEC technology coupled with polymer electrolyte membrane electrolyser developed by WE-NET. By varying the temperature gradient of the sea water from 5 to 25°C, the actual rate of hydrogen production was also varied from 2.5 to 60 Nm^3/h. In another study, Hasan et al. investigated ammonia production for OTEC-integrated plant (14). The system also used a novel integrated thermal management, which was able to boil ammonia at the conditions of −5°C and 0.89 MPa.

The ongoing R&D in Malaysia, particularly in the joint Project of UTM Ocean Thermal Energy Centre and the Institute of Ocean Energy Saga University under the Japanese Science & Technology Agency and Malaysian Ministry of Higher Education funding 2019–2024 of the Science and Technology Research Partnership for Sustainable Development (SATREPS) (8), would look into among others the following R&D components such as the development of nano working fluids to replace ammonia as the conventional working fluid in the transfer of heat from the warm sea water through titanium heat exchanges. It is expected that the outcome of this study would reduce the required temperature differential from 20°C to as low as 10°C, as such the heat from the Sun stored in waters shallower than 800 m could be harnessed and the development of cheaper stainless steel, instead of the expensive titanium, heat exchanges by injecting warm water vapor, instead direct feed of warm seawater, through flash distillation to prevent bio-fouling.

This review article mainly focused on the potential of OTEC-generated hydrogen to produce methanol via CO_2 hydrogenation. Interestingly, the abundance CO_2 can be captured using various capture technologies and the renewable hydrogen can be obtained from the electrolysis of water by utilizing power generated from OTEC. Therefore, this article firstly discussed the CO_2 hydrogenation to methanol using various catalysts to have insight into the catalyst development for this process. In addition, recent development of CO_2 capture technologies, including absorption, membrane separation, cryogenic separation, adsorption, and gas hydrate separation, are also elaborated. Additionally, the conversion of captured CO_2 and the possibility of OTEC power to generate renewable hydrogen for the conversion into methanol is also critically reviewed and supported theoretically using the Aspen HYSIS approach. By employing various catalysts and reaction conditions, the findings showed encouraging results of CO_2 conversion of ≥50% and product yield of ≥80%. These theoretical studies for the direct CO_2 conversion to methanol using OTEC-generated hydrogen showed great research potential and can be further explored in the future.

2. CO_2 hydrogenation into methanol

Stringent environmental legislation and restriction under Malaysia Environmental Quality (Clean Air) Regulations 2014 prompted efforts toward exploring the transition from gray, blue to green hydrogen from renewable resources such as that derived from wind, solar, geothermal, ocean thermal energy, and biomass. These renewable resources offer alternative routes to produce hydrogen for the hydrogenation of methanol. The current route to generate hydrogen is through natural gas reforming and coupled with carbon capture, utilization, and storage to reduce CO_2 emissions (15). The release of carbon dioxide has been increased from 325 ppm in 1970 to 408 ppm in 2018. This increase has led to cause significant environmental problems as the present society is heavily utilizing the fossil-fuel-based energy sources. There are two major impacts of using fossil-fuel-based energy sources on the environment including the accumulation of CO_2 into the atmosphere and shortening the C-reserves for future generations.

The societal high energy demand to maintain the higher standards of life and the impossibility of maintain the standards through usual ways is causing such problems and led to increase the attention of researchers in past few years. Many studies have been done utilizing hydrogen and reduction (recycle or stored) of CO_2 hydrogenation for the past few years and showed a great interest regarding zero-emission. Hydrogen gas is extremely flammable and non-toxic and can be produced through steam methane reforming, coal gasification, and water splitting by electrolysis (16). The conventional feedstocks used to produce hydrogen depend on the synthesizing method as listed in Table 1.

Hydrogen can be utilized as fuel in an engine and utilized to produce methanol by the hydrogenation of carbon dioxide. Hydrogen can easily be found abundantly in nature, especially in water such as brine (seawater), river, rain, or well. Four energy forms are required to extract hydrogen, such as biochemical, photonic, electrical, and thermal processes. Production of hydrogen from renewable energy resources can be applied to the hydrogenation of methanol.

Fernández-Dacosta et al. (6) stated that through the implementation of multiple carbon capture unit, CO_2 utilization and storage, a large CO_2 emission reduction could be achieved by mixing it with hydrogen to produce methanol. The carbon capture, CO_2 utilization and storage technologies drive, a great amount of CO_2 to be reduced for a cleaner and greener atmosphere. Further, the conversion of CO_2 into methanol received

Table 1. Conversion for hydrogen production from various feedstocks.

Feedstock	Hydrogen production (1 kg)
Coal	7.6 kg
Natural Gas	4.5 m^3
Water	11.36 kg

considerable attention due to excessive accumulation of CO_2 into the atmosphere that led to global warming. It was reported that the production of CO_2 from the industrial sector contributed to approximately 3300–3500 Mt/year, which is considered very high (17). Approximately 50% of CO_2 release into the environment took place in the last 50 years (18,19). The governing bodies of G20 countries spend approximately 80–88 billion US dollars every year to subsidize the use of fossil fuel (20). The present reserves of world's coal, oil, and natural gas (the principal CO_2 emission sources) release approximately 2,795,000 Mt CO_2, which is about five folds higher than the appropriate amount that can be released (21). Therefore, it is necessary to mitigate the massive release of CO_2 by converting it into hydrocarbons especially using renewable hydrogen. Currently, hydrogen sources can be obtained from syngas, petrochemical plants, methane steam reforming, and coke gas (22). Several researchers have proposed a technology that involves utilization of renewable energy for CO_2 conversion to produce value-added chemicals. In previous work by Shih et al. (23), solar energy has been utilized as an energy source for CO_2 conversion to methanol. Similarly, the eco-friendly process has been developed by Do et al. (24) for methanol production using direct hydrogenation of CO_2 with renewable hydrogen. This finding indicates that the development of the coupling technology involving the capture of CO_2 and renewable hydrogen has become an interest due to the promising routes for the sustainable and eco-friendly processes.

The downstream processing steps to produce methanol are influenced by the purity of hydrogen and CO_2 depending on the type of reactions involved. The hydrogenation for the conversion of renewable hydrogen and CO_2 through reverse water gas shift reaction to methanol. In advancing the utilization of green hydrogen, through water splitting, its cost competitiveness is important in pushing the technology's attractiveness. Conversion of CO_2 into methanol via hydrogenation is one of the attractive routes. A lot of research has been conducted on the synthesis of methanol from CO_2 using various catalysts. The findings of this study showed superior catalytic activity with 83.9% methanol selectivity and 12.6% CO_2 conversion to methanol. Jia et al. (25) studied the production of methanol using an In_2O_3-supported nickel catalyst that was synthesized using wet chemical reduction with sodium borohydride as a reducing agent. In addition, the temperature effect on the conversion of CO_2 was also studied. A 100% selectivity of methanol was found at a temperature below 225°C. However, the selectivity decreased to 64% beyond 225°C. Ting et al. (26) developed TiO_2 supported catalyst with Re promoted for the selective hydrogenation to methanol and the methanol selectivity was found to be 82% at the optimized reaction conditions of CO_2 and hydrogen pressures of 1 and 5 MPa, respectively, and at the temperature of 150°C.

Samson et al. (27) studied the use of Cu/ZrO_2 catalyst for methanol production and synthesizing the catalyst by the impregnation of ZrO_2 with citric acid. The characteristics of the synthesized catalyst by BET and XRD showed the highest potential to produce methanol. The CO_2 to methanol operating conditions were kept as CO_2/H_2 ratio of 3:1, reaction temperature of 260°C, reaction pressure of 8.0 MPa and GHSV of 3600 h^{-1} resulting in the CO_2 conversion and methanol selectivity of 15% and 86.0%, respectively. Jung Li et al. (28) investigated the effect of Ga^{+3} on the selectivity of methanol in the presence of Cu/ZnO as a heterogeneous catalyst. The introduction of Ga^{+3} promoted, the reduction of Zn^{+2} to Zn^{+0}, which apparently increased the methanol production from carbon dioxide. The operating conditions for the methanation process were kept as H_2/CO_2 molar ratio of 2.8:1, reaction temperature of 240°C, and reaction pressure of 4.5 MPa, resulting in the methanol yield of 50%. Rui et al. (29) investigated the methanation of carbon dioxide using Pd/I_2O_3 as a heterogeneous catalyst. The strong interaction between Pd and In_2O_3 during the catalyst preparation led to the formation of Pd-In bimetallic species. The Pd/In_2O_3 catalyst was prepared by mixing In_2O_3 powder with Pd/peptide composite, which was followed by thermal treatment to remove the peptide. The operating conditions of methanation process were kept at the reaction pressure of 5 MPa, reaction temperature of 300°C, resulting in the overall methanol selectivity of >70%.

Choi et al. (30) investigated the methanation of CO_2 using Pd-Cu/CeO_2 catalyst. Highest methanol yield was obtained by the impregnation of the catalysts, including 10 wt.% of Cu, 1 Pd, and CeO_2 at 210°C. In catalysis, the catalyst support provided to the catalyst causes a significant increase in the activity of the catalyst. Therefore, Lin et al. (31) investigated the use of catalyst support of Pd-Cu for the heterogeneous catalysts, including TiO_2, ZrO_2, Al_2O_3, and SiO_2. Among the TiO_2 supports, commercial TiO_2 P25 supported with Pd-Cu exhibited the highest CO_2 hydrogenation activity and showed CH_3OH selectivity of 25.7%, and CO_2 conversion of 16.4%. Meanwhile, Dong et al. (32) investigated the CO_2 hydrogenation to methanol using Cu/Zn/Al/Zr catalyst calcined at 573 K. The maximum CO_2 conversion of 24.5% and 57.6% of methanol selectivity were obtained at a pressure of 5 MPa, H_2/CO_2 molar ratio of 3:1, reaction temperature of 270°C and GHSV of 4600 h^{-1}. Peng Gao et al. (33) investigated the production of methanol using carbon dioxide by modifying the Zn/Al/Cu catalysts with the help of Mn, Ze, and Y. Results indicated that BET surface area in each case was significantly increased. However, the catalyst modified with Y exhibited the highest production efficiency of methanol. The operating conditions were kept at H_2/CO_2 ratio of 3:1, temperature of 230–270°C, and pressure of 5.0 MPa. This was observed due to significant increase in the surface area of Cu, which in turn increased the number of basic actives sites to the total number of active sites.

Although a rise in temperature encourages CO_2 activation, it also considerably increases the generation of unwanted CO in the water-gas shift reaction, which causes a decrease in methanol's selectivity. Additionally, the presence of water vapor (either from the RWGS or from the hydrogenation process) in the end products may prevent the synthesis of methanol and cause the catalyst to lose its effectiveness by speeding the growth of metal particles in supported catalysts. Three qualities are necessary for the creation of the best CO_2 hydrogenation catalysts: (i) adsorption, activation, and stabilization of CO_2; (ii) dissociation of the H–H bond in H_2 and facilitation of its reaction with the intermediates to produce methanol; and (iii) prevention of the poisoning effect of water on the active sites. The metal and metallic oxides are used as a catalyst in the hydrogenation reaction. The three characteristics can be balanced by using multicomponent catalyst systems, which have at least two interdependent components.

Promising catalysts include oxide-supported metals, which function by forming a particular alloy in supported metal particles or by exerting an interfacial action at the oxide–metal interfaces. Higher active surface area present on the catalyst surface allows the reactants to interact for successful hydrogenation which leads to a higher methanol yield. The effective catalyst which can cause successful hydrogenation must have a higher active surface area, pore volume and diameter, basicity, and interictal affinity toward the reactants to interact. A good catalyst needs to bind tightly enough to the reactant to allow the reaction to occur. The metals are also as a catalyst support along with the other metals/metal oxides as a catalyst. It has been discovered that metal–support interactions can alter the active metallic phase's catalytic properties (such as shape, dispersion, etc.), and hence have an impact on the activity of CO_2 hydrogenation. Crystallite metal loading and size impact supported metal catalysts' catalytic activitydepending on the environment and the metal support combinations. The creation and stabilization of the catalysts' active phase are both impacted by choice of support, although can adjust how the major component interacts with the promoter.

Recently, few studies have been conducted on the CO_2 hydrogenation; Table 2 summarizes the catalytic hydrogenation of CO_2 to green hydrocarbons. Rezayee et al. (34) investigated the production of methanol from CO_2 using a ruthenium catalyst in the presence of dimethylamine. The CO_2 to methanol conversion of greater than 95% was achieved using tandem catalysis. Jiang et al. (35) investigated the production of methanol using a series of catalysts consisting of Pd/In_2O_3/SBA-15 catalysts that were synthesized by the citric acid method. In another study, copper and zinc oxide composite was utilized to produce methanol by keeping the operating conditions of reaction temperature of 250°C, reaction pressure of 3.0 MPa, H_2: CO_2 ratio of 3:1. The overall carbon dioxide conversion of 11% was obtained at the optimized conditions (36). In another study, Samson et al. (27) studied the Cu with ZrO_2 as the catalyst support for the reaction conditions of reaction temperature of 260°C, reaction pressure of 8.0 MPa, H_2: CO_2 ratio of 3:1. 86% of methanol yield was achieved at the optimized conditions with 15% of CO_2 selectivity.

Martin et al. (39) used $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ as a catalyst for the synthesis of methanol via hydrogenation process. The operating reaction conditions were kept as reaction temperature of 250°C, reaction pressure of 5.0 MPa, H_2: CO_2 ratio of 2.8:1. The maximized methanol yield of 99.72% was achieved at these operating conditions. Shen et al. (40) investigated the influence of catalyst loadings of Ir/In_2O_3 in the range of 0–15 wt.%. A maximum CO_2 conversion of 17.7% and methanol yield of 70% at the optimized conditions of high methanol space time yield of 0.765 g MeOH h^{-1} $gcat^{-1}$ at 4/1 of the CO_2/H_2 feed ratio, 21 000 h−1, 300°C, and 5 MPa. With the catalysts tested, the higher Ir loading caused the higher activity. The catalyst characterization confirmed an intense interaction between iridium and In_2O_3, which caused the high dispersion of the Ir catalyst with the Ir–In_2O_3 interface as the active site for selective hydrogenation of CO_2 into methanol. The production of methanol using various metals and metallic catalysts is summarized in Table 2.

In short, hydrogenation of CO_2 into methanol is considered as one of the sustainable processes since it can produce value-added products while at the same time potentially decreasing the global warming. To date, various efficient catalysts have been reported for this process and proven to successfully maximize the yield of methanol. In addition to this, excellent CO_2 technologies are needed to capture sufficient CO_2 for the conversion of CO_2 to methanol. Furthermore, an excellent yet renewable hydrogen source is also essential to supply green hydrogen for the CO_2 hydrogenation process, and this can be done via OTEC in which the

Table 2. Summary of catalytic hydrogenation of CO_2 to green hydrocarbons.

Catalyst	Conditions	Remarks	References
Ruthenium catalyst	–	• CO_2 to methanol conversion of greater than 95% was achieved	(34)
Pd/In_2O_3/SBA-15	$T = 260°C$, $P = 5$ MPa	• 12.6% CO_2 conversion to methanol with 83.9% methanol selectivity	(35)
In_2O_3-supported nickel catalyst	$T = 300°C$	• 100% selectivity of methanol was found at a temperature below 225°C • The selectivity decreased to 64% beyond 225°C	(25)
TiO_2 supported catalyst with Re promoted	$T = 150°C$, $P = 5$ MPa	• Methanol selectivity was found to be 82% at the optimized reaction conditions of CO_2 and hydrogen pressures of 1 and 5 MPa, respectively and at the temperature of 150°C	(26)
Cu/ZrO_2 catalyst	$T = 260°C$, $P = 8.0$ MPa, CO_2/H_2 ratio = 3:1, GHSV = 3600 h^{-1}	• CO_2 conversion of 15% with methanol selectivity of 86.0% were obtained. • The CO_2 to methanol operating conditions were kept as CO_2/H_2 ratio of 3:1, reaction temperature of 260°C, reaction pressure of 8.0 MPa and GHSV of 3600 h^{-1}	(27)
Cu/ZnO	$T = 240°C$, $P = 4.5$ MPa, CO_2/H_2 ratio = 2.8:1	• Methanol yield of 50% was obtained. • The operating conditions for the methanation process were kept as H_2/CO_2 molar ratio of 2.8:1, reaction temperature of 240°C, and reaction pressure of 4.5 MPa	(28)
Pd/I_2O_3	$T = 300°C$, $P = 5$ MPa	• Overall methanol selectivity of >70% was obtained • The operating conditions of methanation process were kept at the reaction pressure of 5 MPa, reaction temperature of 300°C	(29)
$Pd\text{-}Cu/CeO_2$	$T = 210°C$, Pd-amount = 2 wt.%	• Highest methanol yield was obtained by the impregnation of the catalysts including 10 wt.% of Cu, 1 Pd, and CeO_2 at 210°C	(30)
TiO_2 P25 supported with Pd-Cu	–	• CO_2 conversion of 16.4% with methanol selectivity of 25.7% were obtained	(31)
Cu/Zn/Al/Zr	$T = 250°C$, $P = 5.0$ MPa, GHSV = 4600 h^{-1}	• CO_2 conversion of 24.5% with 57.6% of methanol selectivity were obtained	(32)
Zn/Al/Cu	$T = 230240°C$, $P = 5.0$ MPa, CO_2/H_2 ratio = 3:1	• Catalyst modified with Y exhibited highest production efficiency of methanol • The operating conditions were kept at H_2/CO_2 ratio of 3:1, temperature of 230–270°C, and pressure of 5.0 MPa	(33)
$2\%Rh\text{-}2\%Ce/SiO_2$	–	• Methanol selectivity of 12.0% was obtained	(37)
Co_6/MnO_x	$T = 200°C$	• This catalyst avoids the formation of CO intermediate by enhancing the CO_2 adsorption and weakened the hydrogen adsorption on the catalyst	(38)

generated renewable power from OTEC will be utilized in the production of green hydrogen by water electrolysis. Details of the CO_2 capture technologies and OTEC technology will be discussed in the next two sections.

3. Carbon dioxide capturing technologies

Efficient CO_2 capture process is a substantial step prior to CO_2 utilization to ensure a feasible zero carbon emission goal. In past decades, various CO_2 capture technologies have been proposed to capture CO_2 from post-combustion and industrial processes. These technologies include absorption, membrane separation, cryogenic separation, adsorption, and gas hydrate separation. Absorption is one of the most widely used technologies for CO_2 capture as it is a well-established method, and it can recover high purity of CO_2 (41–44). Research and development have been focusing on enhancing the effectiveness of the solvent used in absorption and the intensification of the gas–liquid contactor as the mass transfer is significantly influenced by diffusion rate as well as the thermodynamic capacity of the solvent. The common solvent used for CO_2 absorption is the amine-based solution. Primary and secondary amines such as Monoethanolamine (MEA) and Diethanolamine (DEA) are highly reactive with CO_2 and easy to be regenerated through the heating process (45,46). However, they are highly corrosive, require high regeneration energy, and has limited absorption capacity at 0.5 mol CO_2/mol amine (47). Due to this, a tertiary amine which is methyldiethanolamine (MDEA) attracts the attention of researchers due to its high absorption capacity (1.0 mol CO_2/mol amine) and required less regeneration energy (48,49). However, it has slower reaction kinetics and higher degradation rate as compared to primary and secondary amine (46,50,51). Another alternative solvent is the potassium carbonate (PC). It is less corrosive, non-volatile, environmental friendly and consumes less energy (52,53). The only challenge associated with PC solvent is the slow absorption rate (52,54,55). Thus, the use of rate promoters is recommended by various researchers to enhance the kinetics of PC with CO_2.

Since the conventional packed column has an excessive footprint, the intensification technologies focus on reducing the absorber size by improving the mass transfer performance. One of the intensification technologies is the rotating packed bed (RPB). To enhance the mass transfer and equipment dimension, fine droplets would be produced by high-intensity centrifugal forces (56–59). However, it has a slower reaction kinetics rate as compared to primary and secondary amine (46,50,51). Another intensification technology is the membrane contactor. The gas–liquid membrane possesses high surface area, which resulted in high mass transfer rate across the membrane. The dimension for the contactor can be substantially minimized up to nearly three-quarters as compared to the conventional packed column

(60–63). Membrane has low tendency of flooding, foaming, and channeling (61,62). However, the membrane system might require higher capital expenditure due to regular replacement within the stipulated operating duration. Another promising intensification technology is the ultrasonic-assisted CO_2 absorption system (64–68). The presence of high-frequency ultrasonic irradiation enhances the mass transfer process through its physical and chemical effects, which resulted in absorption enhancement of up to 80-fold (66). This technology potentially offers a smaller contactor volume (up to 12 fold) as compared to the conventional column (64). However, this technology is still under research development stage prior to its commercialization into the industry. Another promising intensification technology is the high frequency ultrasonic-assisted CO_2 absorption system (64–68). The high-frequency ultrasonic system enhances the absorption performance through its physical and chemical effects. The ultrasonic irradiation generates acoustic streaming, fountain, and atomization, which improves the gas–liquid mixing and generates higher gas–liquid interfacial area (66,69–74). Ultrasonic system has been widely used in many industrial applications due to its ability to enhance the mass transfer process. Based on the literature, most of the studies of using ultrasonic irradiation for gas–liquid system were conducted using low ultrasonic frequency of 20–500 kHz (75–81). Studies have shown that low ultrasonic frequency is more efficient in enhancing the desorption process due to the cavitation effect and insufficient enhancement with higher energy requirement was observed for absorption process (76–84). However, recent studies using high-frequency ultrasonic irradiation of 1.7 MHz have shown absorption enhancement of up to 80-fold (66). This is because, theoretically, higher ultrasonic frequency can reduce the cavitation effect due to insufficient time to initiate cavitation (85), thus enhancing the absorption process. This technology potentially offers smaller contactor volume (up to 12-fold) as compared to the conventional column (64). However, this technology is still under research development stage prior to its commercialization in the industry.

Meanwhile, membrane separation is another widely applied CO_2 capture technology because of its benefits such as energy efficiency, modular, and chemical-free operation (85). Recently, the focus on membrane development shifted to a thin-film composite membrane (TFCMs). The most common porous substrate employed in the fabrication of TFCMs are polysulfone (PSF) (86), polyacrylonitrile (PAN) (87,88) and alumina due to their non-resistance to the permeate gas molecule (89). Furthermore, polydimethylsiloxane (PDMS) is extensively utilized for gutter layers owing to its high gas permeability (90,91). The existence of the gutter layer resulted in the minimum defect-free membrane (92) as well as facilitated the transport of gas molecules from the selective layer to the support. The current development of TFCMs can unlock current membrane development's inadequacy for CO_2 separation. Nevertheless, several aspects shall be considered in developing high-performance TFCMs, such as material selection for the three layers of TFCMs, practical methods for TFCMs preparation at the scale-up level, which can accommodate the industrial application, and finally on the stability of the membrane performance. Thus, it is crucial to look in-depth into all these aspects to succeed in TFCMs membrane development. Overall, the development of TFCMs membrane has potential for membrane separation technology, particularly in CO_2 gas separation applications.

Cryogenic or low-temperature CO_2 separation is one of the CO_2 capture technologies that focus on low-temperature CO_2 separation. Under cryogenic conditions, the CO_2 is condensed as a liquid in a distillation column, in which the condensed CO_2 is separated from other lighter gaseous components. This technology is mainly used for bulk CO_2 separation (> 50%), for instance, separation of high-concentration CO_2 from natural gas stream (93). Commercial cryogenic CO_2 separation processes, include Ryan-Holmes process, Controlled Freeze Zone (CFZ^{TM}) process, CryoCell®, SPREX™, etc. have not been widely applied at industrial scale contributed by the constraint of requirement high refrigeration duty and solid formation (94,95). Since the last decade, cryogenic technology has significantly advanced in term of energy requirement via the breakthrough in cryogenic hybrid technologies and optimum process design (96–106). For bulk CO_2 separation, cryogenic technologies require one-third less energy comparing with other CO_2 capture processes (107). Other benefits for cryogenic CO_2 capture are the chemical-free operation, low tonnage value, lower hydrocarbon loss and larger operating envelope for CO_2 composition and pressure (108).

Adsorption is a very potential technology for CO_2 removal due to its low operating cost and low energy requirement. In recent years, adsorption technology is gaining interest among researchers for their investigation on its effectiveness in CO_2 removal. Compared to other technologies, adsorption technology commonly uses solid adsorbents with low cost and low toxicity. The regeneration process for the solid adsorbents is also easy (109). There are numerous numbers of porous adsorbents potential for CO_2 adsorption, which include mesoporous silica materials, metal organic frameworks materials, activated carbon, zeolite materials, etc. (110–

114). Different characteristics are possessed by these materials to be used as adsorbents. Mesoporous silica materials are widely applied in different fields, including for gas adsorption. There are number of works reported on investigating different mesoporous silica materials for CO_2 gas adsorption, including the works reported by Kishor et al. (115) and Wang et al. (116). There are generally one-dimensional, two-dimensional, and three-dimensional pore structures of mesoporous silica materials. The gas diffusion resistance in one-dimensional and two-dimensional pore structure of mesoporous silica materials is higher than that of three-dimensional pore structure of mesoporous silica materials. The type of pore structure of the mesoporous silica materials is one of the important factors to be considered in the selection of good mesoporous silica materials as CO_2 adsorbent, as it will influences the CO_2 gas diffusion in the pore framework.

The separation of gases via hydrate formation is another emerging technique that can be utilized for CO_2 capture. This method is less energy intensive and able to treat the multicomponent gaseous stream with a high concentration of CO_2. Seo et al. studied the phase behavior and structure of $CO_2 + N_2$ hydrate in the solid bed of silica gel. Their analysis showed that by a three-stage hydrate formation, the purity of captured CO_2 by hydrate crystals could reach to 96 mol% from flue gas with an initial CO_2 content of 10 mol% (117). Later, Duc et al. studied the separation of $CO_2 +$ N_2 in the presence of TBAB. According to this study, the presence of TBAB decreased the hydrate phase boundary of N_2 to drastically lower pressures and consequently, the mixed hydrate of $CO_2 + N_2$ could form at the much milder condition (118). However, the reported separation efficiency was not comparable with previously mentioned studies. Linga et al. chose THF as a promoter for CO_2 + N_2 and CO_2 + H_2 separation (119,120). Their results indicated that hydrate formation has a good potential for capturing carbon dioxide in the system. The uptake gas by hydrate was enriched in CO_2 for $CO_2 + N_2$ and $CO_2 + H_2$ systems (119,120). Linga et al. showed that the recovery (split fraction) of CO_2 can be reached to approximately 42% for both pre-combustion and post-combustion CO_2 capture (119). Li et al. tried to use TBAB as promoting agent for post-combustion capturing of CO_2 (121). Their results indicated that the presence of 5 wt.% TBAB in the solution brings down the operational condition to a feasible condition. In addition, the hydrate formation rate is increased by increasing the pressure (121). Babu et al. used silica sand as the solid bed for CO_2 capture in a post-combustion application. They claimed that the utilization of silica sand is more efficient compared to silica gel (122). Recently, Partoon et al. introduced a new gas hydrate reactor that eliminated the induction time requirement for hydrate formation. The reactor is tested in a gas hydrate lab-pilot plant and the results showed that the gas hydrate formation rate was enhanced more than 20 times compared to the previous reactor without using any KHP additives (123). Table 3 summarizes the benefits, current developments, and research gap/ future direction for the relevant CO_2 capture technologies.

4. Ocean thermal energy conversion (OTEC)

Ocean receives huge radiant energy from the Sun, which heats up the ocean's surface water. The surface temperature profile of the ocean gradually decreases with depth from the exponential decrease of light energy following Lambert's law, making the bottom layer cooler, with further cooling caused by the flow of heavier bottom polar water at 4°C. Thus, a temperature differential is caused in the ocean between the warm surface layer water and cooler bottom layer water. This opens the scope of generating power using a thermodynamic cycle. Power generation from such method is termed as ocean thermal energy conversion (OTEC) system. Because of the high specific heat of water, the surface temperature of the ocean is mostly retained during the night as well, assuring round a clock supply of power from OTEC. This body of knowledge was discovered in 1881 by a French Physicist.

Because of the wave movement, there remains a surface temperature core up to around 100 m depth, and the temperature differential between this surface temperature core with its cooler bottom layer from 600 to 1000 m depth has been noted to be around 10–25°C, respectively (133). Obviously, this temperature differential would be higher in lower latitude regions. It had been estimated that heat energy available from 60 million sq. km. of tropical seas could be equivalent to 250 billion barrels of oil (134). The broad principles of such power generation could be either, by using a low boiling fluid to get evaporated from heat exchanger in contact with warm sea water and run a low-pressure turbine for power generation. Thereafter the fluid may then be allowed to condense encountering cold sea water and thus completing the thermodynamic cycle. Or, instead of the working fluid, the warm sea water itself may be vaporized in low pressure chamber and run the low-pressure steam turbine for power generation. The former is termed 'closed cycle' or, CC-OTEC, and the latter called 'open cycle' or OC-OTEC. The additional benefit derived from the latter, where surface sea water is allowed to evaporate, is the scope of availability of pure desalinated water as a byproduct.

Table 3. Summary of the current CO_2 capture technologies.

Technology	Advantages	Disadvantages	Current Development	Research Gap/Future Direction	Reference
Absorption	High removal efficiency with moderate energy requirement	MDEA and PC demonstrated slower absorption rate as compared to MEA and DEA. The solvent performance can be improved by rate promoters to enhance its reaction kinetics	• Current solvent developments have been shifted from primary (MEA) and secondary amine (DEA) into tertiary amine (MDEA) due to higher absorption capacity and lower regeneration energy requirement • Intensification technologies such as RPB, membrane and ultrasonic assisted CO_2 absorption system have reduced the footprint requirements of the conventional packed column by increasing the gas-liquid interfacial area	Further research on the materials development for membrane contactor is critical to increase its robustness to avoid regular replacement. Ultrasonic assisted absorption shows remarkable reduction of contactor footprint. Yet, more research and pilot validation are required prior to its commercial application	(45–68)
Membrane	Energy efficient, modular and chemical free operation	Pre-treatment requirement	• Research developments have been focusing on improving the membrane materials from polymeric membrane, inorganic membrane, composite membrane until the latest development, which is TFCMs • The materials development aimed to overcome the trade-off issue, improving the chemical and thermal properties as well as the lifetime of the membrane	TFCMs membrane development is essential to improve its performance by enhancing the materials properties, preparation method and stability of the membrane performance.	(85,92,124–126)
Cryogenic	Efficient for bulk CO_2 separation (>50%), chemical free operation, low tonnage value, lower hydrocarbon loss and larger operating envelope for CO_2 composition and pressure	The commercial cryogenic processes have not been widely used in industry due to its high refrigeration duty and solid formation.	Hybrid cryogenic process and optimum process design are the latest advancement of cryogenic technology that managed to reduce the high energy requirement of the commercial cryogenic processes	Cryogenic technology can be further advanced by optimizing the process design to reduce its energy consumption.	(93–108)
Adsorption	Suitable for low concentration CO_2 gas stream with lower operating and energy requirement	Large columns are required as compared to absorption, potential of rapid adsorbent deactivation and longer desorption time	Potential adsorbents for CO_2 capture include mesoporous silica materials, metal organic frameworks materials, activated carbon and zeolite materials	The adsorption technology can be enhanced by improving the adsorbent materials in such a way that it can provide high surface area, good interconnectivity in the pore framework and high affinity to the desired gas molecules	(109–116,127)
Gas Hydrate	Able to treat high CO_2 multicomponent gaseous stream with lower energy requirement	Less matured technology with no commercial application	• The research advancement of hydrate technology has explored various type of promoting agents, which include silica gel, TBAB, THF and silica sand. The addition of the promoting agent aimed to enhance the separation process as well as bringing down the operational condition to a feasible condition • The development in novel gas hydrate reactor system has enhanced the gas hydrate formation rate 20 times higher as compared to the common reactor without using any KHP additives	Further research and testing on the novel gas hydrate reactor system are required to validate its performance prior to its commercial application	(117–123,128–132)

There could also be a third method of power generation; with a combination of both CC-OTEC and OC-OTEC, which is termed Hybrid Cycle OTEC (H-OTEC).

In CC-OTEC type of OTEC a low boiling fluid like liq. ammonia (boiling point 33.5°C at 1.013 bar) is allowed to vaporize when exposed to warm surface- sea-water passed through a heat exchanger (135). The expanded vapor runs a turbine which in turn produces power through a generator. Japanese researchers, however, suggested the use of low-boiling non-azeotropic mixtures of ammonia and water (136). Besides ammonia, low-boiling hydrocarbons, like, propane, propylene may also be used as working fluid for such OTEC types (137). For OC-OTEC tropical seawater is vaporized by flushing it through a spout in a low-pressure chamber which in turn runs a low-pressure turbine to produce power through a generator. It may be noted that boiling point of water is reduced to 26.4°C, when its super incumbent pressure is reduced to 0.03 bar (Engineering toolbox, Pressure, and boiling points of water). But only a small fraction, around 1% to 0.5% of the bulk of water sprayed in the evacuated chamber gets evaporated at 0.03 bar pressure.

Because the latent heat of evaporation is drawn from the bulk of the warm sea water, making it cool off with cessation of further boiling. The use of water has the additional advantage of producing potable water as the by-product of the condensation of the low-pressure steam generated. But gases like, O2, N2, and CO2, which remained in dissolution with sea water, would come out of solution during evaporation which are exhausted out from the condenser, which otherwise lessen its efficiency. In H-OTEC type schemes, the first stage is operated using CC-OTEC type using a low boiling fluid (Ammonia) for power generation. In the 2nd Stage operation warm surface sea water evaporation in a vacuum chamber is made like OC-OTEC operation, mainly for the production of desalinated potable water. All such OTEC schemes may be either on-shore or, off-shore-based types. The former requires much longer cold-water pipes to reach the required depth (600–1000 m); whence the latter requires much longer sub-marine cable lines, of around 1–15 km, depending on the site concerned, for transmitting power incurring huge cost involvement. Hence, it has been suggested to produce hydrogen in the OTEC plant ship itself, utilizing the power generated from the OTEC (138), which also finds use as a renewable energy resource with the scope of power generation using fuel cell.

The challenges faced in OTEC schemes are

- low power generation efficiency because of only a small temperature differential of the thermodynamic cycle used for power generation (Rankine cycle mostly),
- plant stability from tropical storms etc. particularly because of the overhanging long (600–1000 m) cold water pipe,
- Bio-fouling coating formed over metal surfaces, thus lowering the efficiency of heat exchangers, and of course the corrosion from seawater.

OTEC is the only renewable energy system, which requires power for power generation bringing in the question of net electricity available from the gross electricity produced. The optimized commercial plant is required to maintain net power to be 0.7 of the gross power produced. It could be noted from thermodynamic and heat transfer consideration that with a minimum temperature difference of 20°C, around 4 m^3/s warm water is to be passed per MW net electricity production. And the optimum ratio between warm ocean surface water with bottom layer cold water would be around 1.6:1. Japanese researchers suggested preheating the working fluid using solar irradiation, making modified OTEC schemes termed SOTEC (139), which enhances the power conversion efficiency of OTEC. To ensure better stability of OTEC plants, it has been suggested to attach the platform holding the pipe to be flexible enough, like those fitted for the oil drilling industry, where the platform swings under sea-state conditions, keeping the drilling pipes stationary. Likewise, for OTEC, the platform might be allowed to heave during storms, without much affecting the joints of the cold-water pipes. Being supported with cables, these pipes (usually HDPE pipes) may also be detached from the main structure or the platform and are thus saved. This approach, however, has much scope of further improvement from R&D studies. Biofouling problems may be tackled by periodic Chlorine injection as well as mechanical brushing over the heat exchangers, during their maintenance.

Electricity generated from OTEC has been suggested to be utilized for the production hydrogen splitting water by electrolysis, where ECPB (electron-coupled proton buffer) is used for the best yield (140). Obviously, oxygen (eight times the volume of hydrogen) would simultaneously be generated along with the hydrogen. It has also been estimated that at 100% efficiency of the electrolyser, it would require 39kWh with 8.9 L of water, producing 1 kg of hydrogen. But with commercial electrolyser systems, having efficiencies at 56–73%, it requires 70.1–53.4 kWh to produce 1 kg of hydrogen at 25°C and 1 atmosphere pressure. 4.33 kWh is reported to produce 1 NM^3 of hydrogen ($NM^3 =$ meter cube at normal temperature and pressure), which is equivalent to 48.5 kWh/kg. This value corresponds to the electrolyser efficiency of around 61%.

There are many fold advantages of OTEC. They are:

- Availability of potable water from OC-OTEC and H-OTEC
- Scope of availability of mineral enriched water from bottom layer ocean water for all types of OTEC
- Enhanced growth of marine species, including weeds, etc.
- Sequestering of CO_2 increasing ocean's CO_2 dissolution potential.
- Prospect of using cold bottom layer ocean water for cold storage, and refrigerant purpose without power requirement from them
- Scope of producing chemical hub H_2 production and H_2 enriched chemicals.
- Lithium extraction for long-life lithium batteries.

These byproducts make OTEC an economically feasible energy resource with huge economic benefits. Economy is the most important aspect which determines the deployment of renewable energy systems. OTEC has a high capital cost, but its LCOE (Levelized Cost of Electricity) is comparable to that of fossil fuel because of huge by-product availability from OTEC schemes. LCOE is the minimum average price at which electricity is to be sold so that it can cover all the expenditures of the project in its entire lifetime

$$\mathrm{LCOE} = (\mathrm{CRF} * \mathrm{Capex} + \mathrm{Opex})/E_t \tag{1}$$

$$\mathrm{CRF} = i * (1 + i)^N / ((1 + i)^N - 1) \tag{2}$$

where,

CRF = Capital recovery factor %

Capex = Capital expenditure US $

Opex = Operational & Maintenance % of Capex US$ /yr

E_t = Produced electricity in time t

N = Lifetime in years

i = interest rate.

The LCOE of OTEC depends upon project lifetime, interest rate, capex and opex. The size of the plant determines the cost of the electricity also. More the size of the plant less is the cost of electricity. 10MW cost of electricity varies from 0.15 US$.kWh to 0.67 US$/kWh, where 100 kWh varies from 0.03US $/kWh to 0.29US $/kWh. Banerjee et al. opined that for third /third generation of improved OTEC schemes, the advantages derived from its various by-products could be so huge, where the cost of electricity could be even less than fossil fuel power plants (137). As shown in Figure 1, other than that of the Salinity Gradient, the cost of electricity generated by OTEC is the lowest of all sources of renewable energy (8).

From Figure 2, it can be observed that renewable hydrogen can be generated by using the OTEC process which further results in the production of methanol, gasoline, and aromatics. Before the hydrogenation process, it is stored and transported. The storage of hydrogen is costly and has a lot of challenges. Hydrogen possesses low energy density by volume in comparison with other fossil fuels, due to which it is stored in either low-temperature and high-pressure vessels or hydrogen-attracting materials are used. The hydrogen storage techniques are summarized in Figure 3.

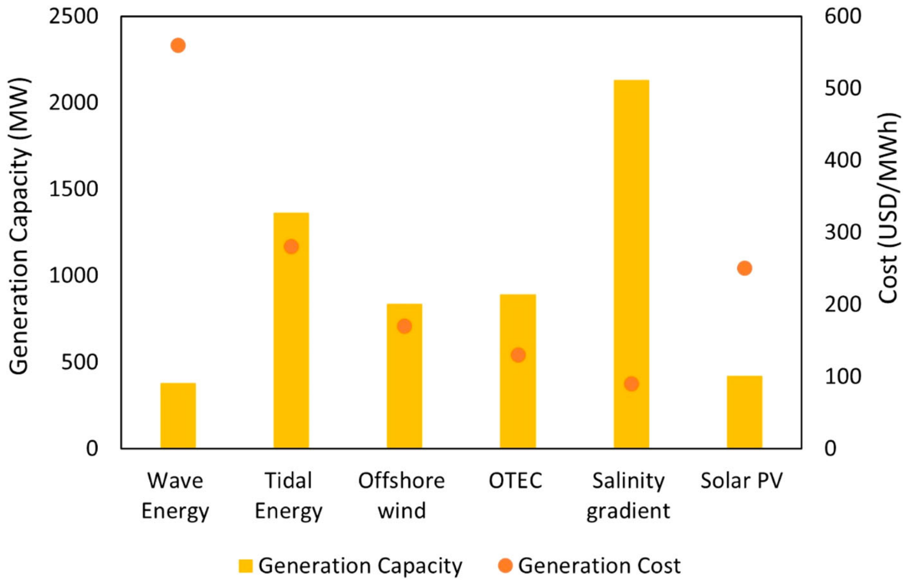


Figure 1. Cost of renewable energy generation by capital investment (8).

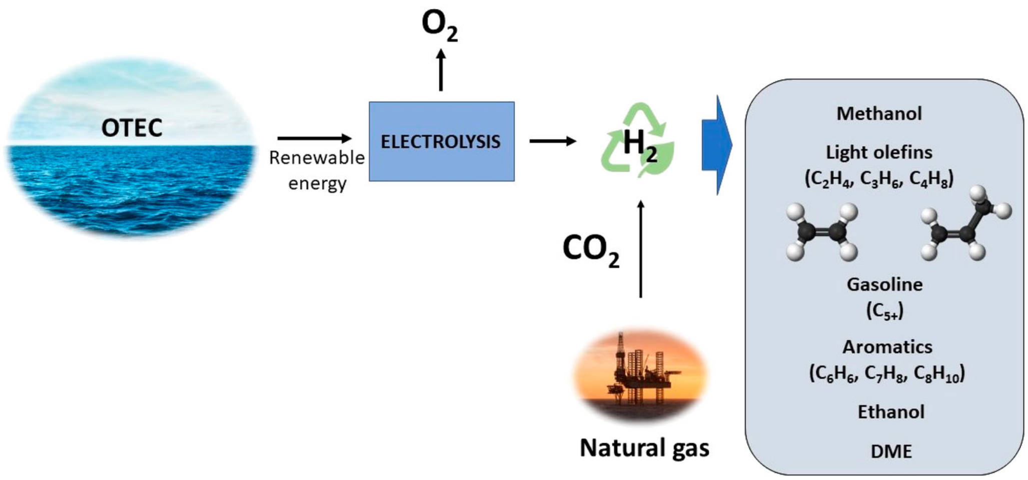


Figure 2. OTEC-based energy for the conversion of CO_2 to value-added hydrocarbons.

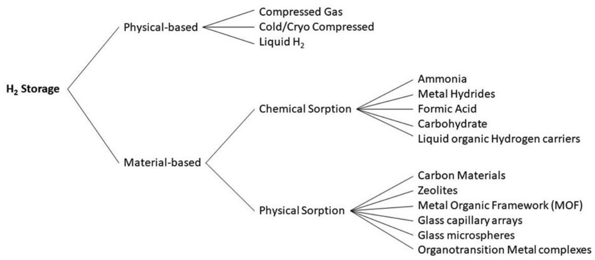
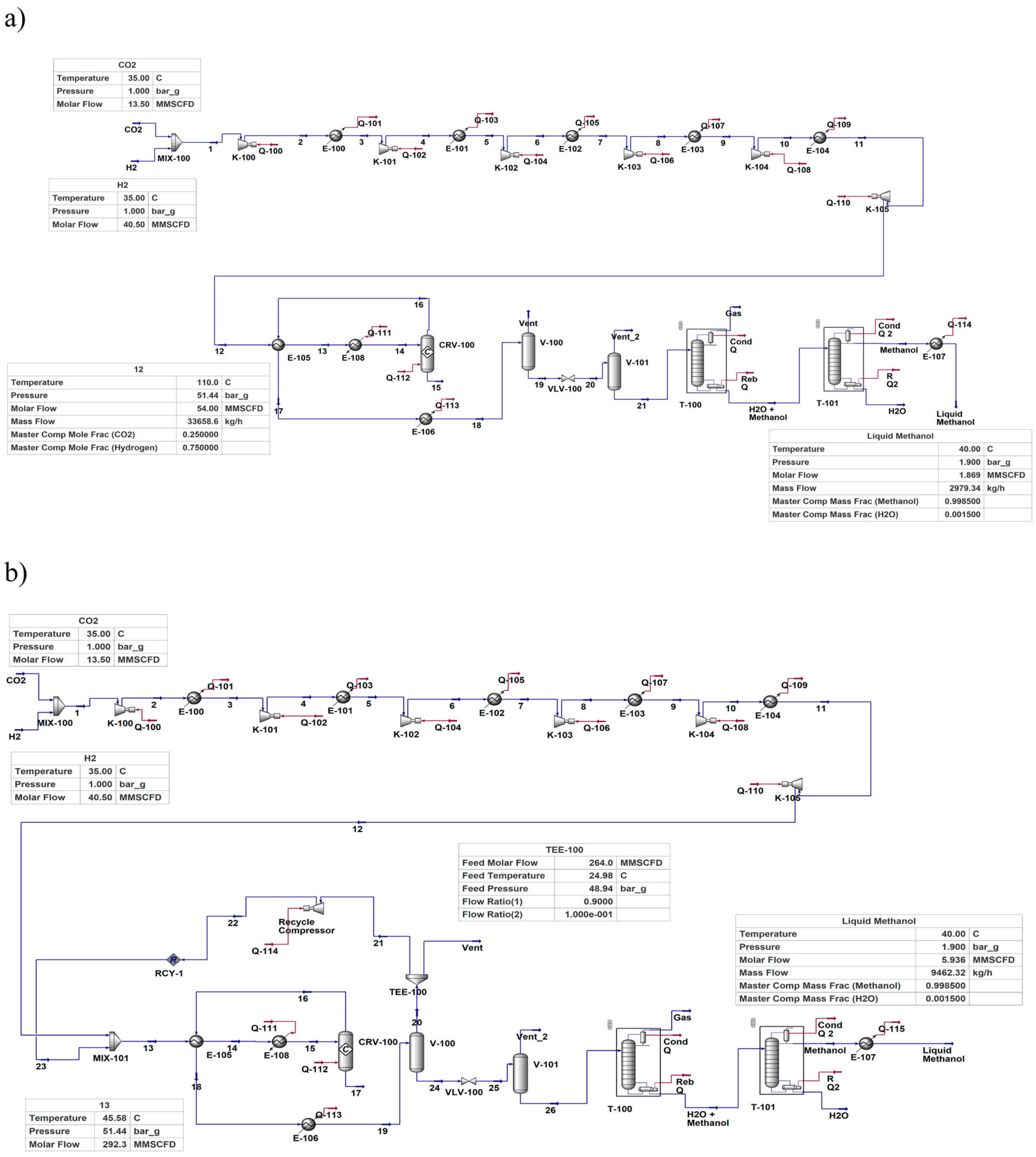


Figure 3. Hydrogen storage techniques.

Figure 3 shows the storage techniques which are used to store and transport the hydrogen. Hydrogen is transported in the form of compressed hydrogen gas stored at high pressure. Liquid/cryogenic hydrogen requires the storage of hydrogen to be done at low temperatures. In this type of storage, liquefaction is done, which is both time and energy-consuming process. In chemisorption, hydrogen is firstly converted into some other hydrocarbons such as ammonia, formic acid, methyl hydrides, etc. before its storage toward the place of its use. The hydrocarbons are again converted back into hydrogen at the point of use.

Feeding into PETRONAS commitment to net zero carbon emission by 2050 (141), the OTEC concept has the potential to tackle the carbon dioxide emissions from deep waters, e.g. block H (142) offshore Malaysia augments. With the target gas production capacity of 270 million standard cubic feet per day (MMSCFD), estimated CO_2 emissions can reach up to a maximum of 755 t/day. One of the approaches to manage the CO_2 generated under deep waters is to combine with hydrogen (143) generated *in situ* from seawater (144) to yield value-added products such as methanol (145,146). Theoretical equilibrium conversion on methanol-based production on Gibbs free energy shows that the methanol yield is 23% at 50 bar, 270°C. However, the results from the experimental catalytic conversion of CO_2 to methanol indicated the yield reduced to 14% tested using a high-pressure fixed-bed reactor (32,147) . This may be due to the reaction kinetic limitation of the reaction and product competition. According to Dong et al., the Cu/Zn/Al/Zr catalysts were used to study the CO_2 hydrogenation to methanol performance at 5 MPa, 270°C with CO_2: H_2 ratio 1:3. They found out that from direct CO_2 conversion to methanol, the primary product obtained is methanol, and the secondary product is carbon monoxide (CO). A CO_2 conversion of 24.5% was accomplished with methanol and CO selectivity of 57.6% and 42.4%, respectively. Hence the yield of methanol is 14.11%, while the CO yield is 10.39%.

One of the main operating parameters to suppress the CO synthesis is reaction temperature. Pavel et al. stated that CO formation is favored at the higher reaction temperature, which will reduce the methanol selectivity while increasing the overall CO_2 conversion (148). This finding is consistent with other literature reported so far (147,149,150). Process simulation was used to estimate the methanol production via commercial software Aspen HYSYS V11. The Peng-Robinson-Styjek-Vera (PRSV) equation was used to establish the thermodynamic properties of gases and polar compounds (methanol and water) for methanol production (151). The catalytic process of CO_2 hydrogenation occurred in the reactor at high pressure (5 MPa) and temperature (270° C). The possible CO_2 hydrogenation reactions were considered as listed below in this simulation. The yield of each product acts as input for the conversion reaction. The conversion of CO_2 to methanol and reverse water gas shift (RWGS) was set at 14.11% and 10.39%,



a)

CO2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	13.50	MMSCFD

H2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	40.50	MMSCFD

12		
Temperature	110.0	C
Pressure	51.44	bar_g
Molar Flow	54.00	MMSCFD
Mass Flow	33658.6	kg/h
Master Comp Mole Frac (CO2)	0.250000	
Master Comp Mole Frac (Hydrogen)	0.750000	

Liquid Methanol		
Temperature	40.00	C
Pressure	1.900	bar_g
Molar Flow	1.869	MMSCFD
Mass Flow	2979.34	kg/h
Master Comp Mass Frac (Methanol)	0.998500	
Master Comp Mass Frac (H2O)	0.001500	

b)

CO2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	13.50	MMSCFD

H2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	40.50	MMSCFD

TEE-100		
Feed Molar Flow	264.0	MMSCFD
Feed Temperature	24.98	C
Feed Pressure	48.94	bar_g
Flow Ratio(1)	0.9000	
Flow Ratio(2)	1.000e-001	

Liquid Methanol		
Temperature	40.00	C
Pressure	1.900	bar_g
Molar Flow	5.936	MMSCFD
Mass Flow	9462.32	kg/h
Master Comp Mass Frac (Methanol)	0.998500	
Master Comp Mass Frac (H2O)	0.001500	

13		
Temperature	45.58	C
Pressure	51.44	bar_g
Molar Flow	292.3	MMSCFD

Figure 4. Process flow diagram of CO_2 conversion to methanol (a) Single path reaction, (b) recycling system (24,151,152).

respectively (105).

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{298K} = -49.5 kJ/mol \qquad (3)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \; \Delta H_{298K} = 41.3 kJ/mol \qquad (4)$$

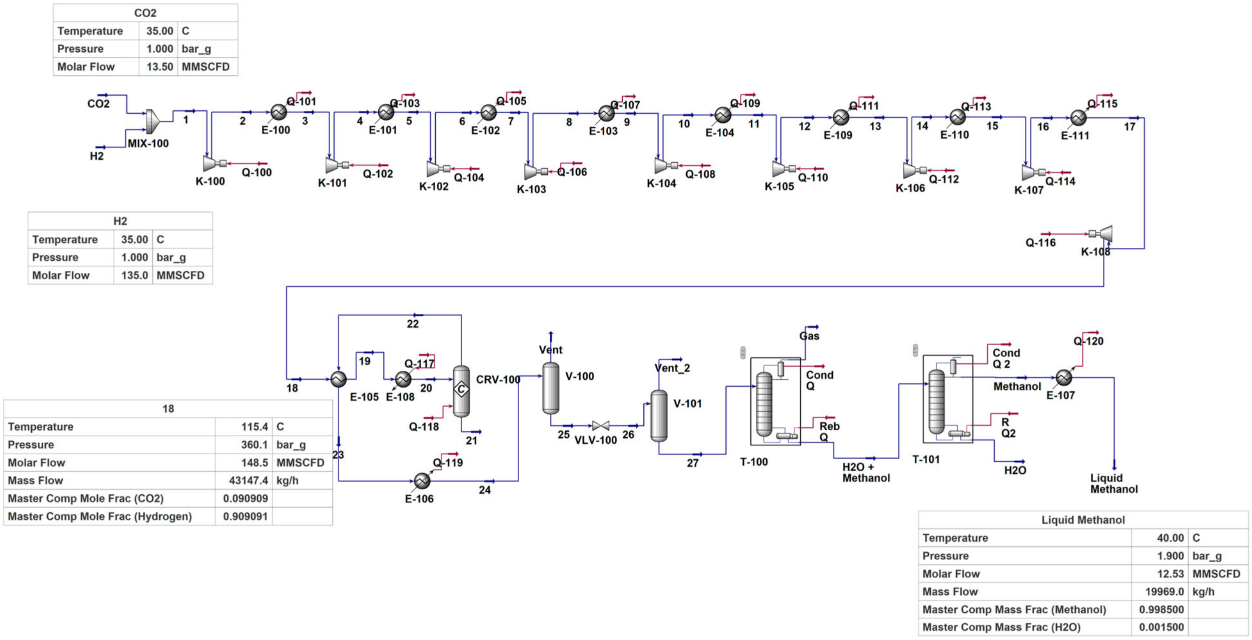
Methanol process flow diagrams are illustrated in Figure 4. There are four cases considered in this study. The key difference for all the cases is on unreacted gases at the recycling system; single path reaction, 90% recycling, 95% recycling, and 99% recycling. Figure 4(a) illustrates the process flow diagram of single-path methanol production. The CO_2 and H_2 gas were mixed (MIX-100) before feeding to the compressor. The binary gas was compressed to 50 barG via six stages of the compressor (K-100 - K105) with five intercoolers (E-100 - E014). The feed gas stream was preheated by exchanging the heat with the product stream in a heat exchanger (E-105) due to an exothermic process and further heated to 270°C using steam. There were TWO reactions involved in the conversion reactor (CRV-100), which are methanol production and RWGS. The product stream with unreacted reactants was cooled down to 25°C using chilled water before the phase separation occurred in the 2-phase separator (V-100). The unreacted gas was vented or can be used as fuel gas. The pressure of the liquid stream was reduced using a pressure-controlled valve (VLV-100) to 3 bar. Any remaining gas is further vented through a 2-phase separator (V-101), while the liquid product enters the purification process to separate the remaining gases (T-100) and methanol purification process at the distillation column (T-102). The theoretical trays at the first distillation column (T-100) were 4, while the second distillation column used 11 theoretical trays to purify methanol to 99.85 wt.%. The temperature of the methanol product was further reduced to 40°C and ready for storage.

Figure 4(b) presents the recycling system's process flow diagram for methanol production. The CO_2 and H_2 gas were mixed (MIX-100) before feeding into the compressor. The binary gas was compressed to 50 barG via six stages of the compressor (K100–K105) with five intercoolers (E100–E014). The feed gas stream was combined with a recycled flow rate before being preheated by exchanging the heat with the product stream in a heat exchanger (E-105) due to an exothermic process and further heated to 270°C using steam. There were two reactions involved in the conversion reactor (CRV-100), which are methanol production and RWGS. The product stream with unreacted reactants was cooled down to 25°C before the phase separation occurred in the 2-phase separator (V-100). According to the cases stated before, the unreacted gas was recycled at 90%, 95% and 99%. The remaining unreacted gas was vented out. The pressure of the liquid stream was reduced using a pressure-controlled valve (VLV-100) to 3 bar. Any remaining gas is further vented through a 2-phase separator (V-101), while the liquid product enters the purification process to separate the remaining gases (T-100) and methanol purification process at the distillation column (T-102). The theoretical trays at first distillation column (T-100) were 5, while the second distillation column used 13 theoretical trays to purify methanol to 99.85 wt.%. The temperature of the methanol product was further reduced to 40°C and ready for storage.

Methanol productions were based on two scenarios; single path route and the addition of a recycling stream to compare the effect on recycling within methanol production. Purging is necessary to remove inert compounds and avoid any accumulation that will impact the methanol conversion performance. The purging percentage is governed by the amount of inert and by-products build-up at the conversion reactor. The typical by-products of CO_2 hydrogenation to methanol are CO, methane (CH_4), methylformate, dimethyl ether, etc. Methanol production at a variation of recycling percent for CO_2:H_2 at 1:3 ratio. The recycling rate of unreacted reactants is vital to improve methanol production and reduce the overall production cost. The production of methanol, with the inclusion of recycling, generated 3–4 times higher production than that of a single path route.

Researchers also investigated the effect of an excess of H_2 in methanol synthesis performance (81,153). Banded and Urakawa (153) found that with an excess of H_2, the methanol yield was impressively improved up to 93.10% with a selectivity of 98% and CO_2 conversion of 95%. This study was carried out with CO_2: H_2 ratio of 1:10 at 360 bar and 260°C. This finding is consistent with theoretical equilibrium conversion, which is at 95.63%. They stated the methanol production process with a feed ratio of 1:≥10 operating in a thermodynamic system will reach the equilibrium CO_2 conversion to methanol. The feed ratio less than 1:10 is under the kinetic regime as the dominant role. Figure 5 presented the methanol production estimation at 36 MPa and 260°C using the same concept of the previous simulation, but with CO_2: H_2 ratio of 1:10 and with additional compression energy. The CO_2 conversion to methanol is set at 93.10% at the conversion reactor. Due to high CO_2 conversion, recycling is not considered in this case. The excess of H_2 is separated at a 2-phase separator. This excess of H_2 at the vent stream can be used as a feed to other CO_2 conversion systems as a 2-step or 3-step CO_2 conversion system to produce valuable products. Based on the simulation done, the single path methanol production is 478.54 MTPD (19,969 kg/h) and almost double that previous recycling system. This high methanol production is contributed by high CO_2 conversion and higher methanol selectivity. From the economic point of view, a higher methanol yield with a low recycle ratio will have a better economic. However, at the operating pressure of 36 MPa and 1:10 ratio of the feed gas, it is hard to be commercialized. These are due to the high compression energy required, special material to sustain at high operating pressure, and H_2 ratio of 10, significantly impacting the project's overall techno-economic because the current price of H_2 is quite expensive. The system integration of CO_2 conversion to valuable products with an excess of H_2 from the methanol production process is possible to improve the overall system's technoeconomic.

In this study, the H_2 supplied for direct CO_2 to methanol is assumed using electrolysis technology by water splitting. The cell efficiency of electrolysis results in 50 kWh of electricity required to produce 1 kg of H_2



CO2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	13.50	MMSCFD

H2		
Temperature	35.00	C
Pressure	1.000	bar_g
Molar Flow	135.0	MMSCFD

18		
Temperature	115.4	C
Pressure	360.1	bar_g
Molar Flow	148.5	MMSCFD
Mass Flow	43147.4	kg/h
Master Comp Mole Frac (CO2)	0.090909	
Master Comp Mole Frac (Hydrogen)	0.909091	

Liquid Methanol		
Temperature	40.00	C
Pressure	1.900	bar_g
Molar Flow	12.53	MMSCFD
Mass Flow	19969.0	kg/h
Master Comp Mass Frac (Methanol)	0.998500	
Master Comp Mass Frac (H2O)	0.001500	

Figure 5. Process flow diagram of CO_2 conversion to methanol at 36 MPa, 260°C with CO_2: H_2 ratio of 1:10.

(154,155). In this work, the renewable electricity source is theoretically from OTEC technology and is used to produce renewable H_2. The capacity of renewable energy generated by OTEC is approximately 1000 MW (6). Because of 13.5 million Standard Cubic Feet Per Day, MMSCFD of CO_2 available for the methanol production process, 204 MW of OTEC power is theoretically required to generate 40.5 MMSCFD (97.82 MTPD) of hydrogen that is required for methanol production, if CO_2:H_2 ratio of 1:3 is used. This power requirement is much lower in comparison with CO_2:H_2 ratio of 1:10 in which 678, 000 KW power is required. Hence, the electricity capacity generated from OTEC can cover the electrolysis power requirement to produce hydrogen up to the ratio of 10. Although the production of methanol is double for CO_2:H_2 ratio of 1:10, but the much higher power requirement of more than double will impact the economics of this route and further economic evaluation is required. Other important criteria, such as the utilization of excess H_2, high-pressure equipment requirement, etc. are among the important criteria to also be considered in economic evaluation.

5. Conclusions and future recommendations

Clean energy and CO_2 conversion technologies have progressed drastically over the past decades. Many CO_2 capture technologies that had been utilized in reducing the harmful effects of CO_2 emission. Based on the current review, the following findings have been observed.

- These separation technologies, such as absorption, membrane and cryogenic separation, adsorption, and hydrate formation, had progressed significantly in the past decades. Nonetheless, the percentage of adoption of CO_2 capture technologies is still required to be increased. On the other hand, hydrogen as a clean and efficient energy source had also been explored extensively to support clean energy utilization.
- Direct hydrogenation of CO_2 by using renewable hydrogen from OTEC can lead to cheaper and greener hydrocarbon production. Synergies between the current refineries process and renewable hydrogen generation from electricity generation from OTEC technology open opportunities to generate methanol and green hydrocarbons.
- Further techno-economic analysis on the integration between CO_2 conversion to valuable products in excess of renewable H_2 to be further explored to progress toward its commercialization potential. This can be done by using the simulation tools such as Aspen HYSYS or Aspen PLUS to study the overall feasibility of the process.

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