

Prospect of Direct Dimethyl Ether Production from CO₂: Reactor Design Development

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Abstract The increasing emissions of carbon dioxide (CO₂) and volatile hydrocarbons via burning of fossil fuels result in a significant amount of global warming and air pollution. With the concern over the impact of fossil fuel to the environment, the interest in alternative fuel production from the CO₂ generated through utilization of new technologies has risen rapidly. Several clean alternative fuels, including dimethyl ether (DME) have been investigated for a more sustainable and greener environment. DME has a high cetane number but produces much lower NO_x emission upon combustion. DME is typically synthesized using syngas based on conventional indirect DME route, where the process begins with conversion of syngas into methanol and subsequently dehydrated to DME in separate units. Recently, a direct single-step route to produce DME through dehydrogenation of CO₂ and dehydration of methanol by utilising a novel bifunctional catalyst has been investigated. In direct DME, the dehydrogenation and dehydration occur simultaneously in a single reactor, which eliminate the need for a methanol production plant. However, the use of conventional fixed-bed reactor (FBR) for the direct DME synthesis causes many challenges including catalyst deactivation, where water appears in the reaction area, limiting the conversion of CO₂ reactants into DME and consequently, the DME yield. It is also essential to manage the exothermic heat generated from the catalyst for better DME yield. In order to overcome these hurdles, several types of reactors have been proposed such as fluidized bed reactor, slurry reactor, microreactor and catalytic membrane reactor. In this paper, different types of reactors are first discussed and its applications related to the direct DME production from CO₂ are highlighted. Finally, the challenges and difficulties of reactor development are addressed and future direction is outlined.

Keywords: Dimethyl ether, syngas, reactor design, fixed bed reactor, fluidized bed reactor, membrane reactor, process intensification.

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Introduction

Fossil fuels remains essential to the world's energy supply and transportation sectors, despite the rapid development of renewable energy sources. The burning of these fossil fuels, especially those that contain carbon, emits large amounts of CO₂. Consequently, this contributes to sea level rise, climate change and ocean acidification [1]. In Malaysia, the CO₂ emission showed a significant increase from 14.7 to 26.2 million tonnes between 1971 and 2020 [2]. As a result, there is an urgent need to tackle the

CO₂ emissions to meet the global climate goals. Among the techniques proposed includes carbon capture and storage (CCS), which involves the capture of CO₂ from various industries before being transported and stored deep underground. However, there are several technical and economic difficulties faced by the CCS, including large capital investment and uncertainty in CO₂ leakage rates. In some countries where geological storage capacity is limited or only accessible offshore, the CCS cost could become very expensive due to huge transportation and injection costs. Recently, carbon capture and utilisation (CCU) has drawn worldwide attention as it is capable of turning the CO₂ waste into useful resources like chemicals and fuels, while also assisting in the mitigation of climate change, making it profitability endeavour [3]. As a conventional petrochemical feedstock, CO₂ has benefits to be a 'renewable' resource since it is continually being emitted by various industrial activities, non-toxic and low costs (Figure 1).

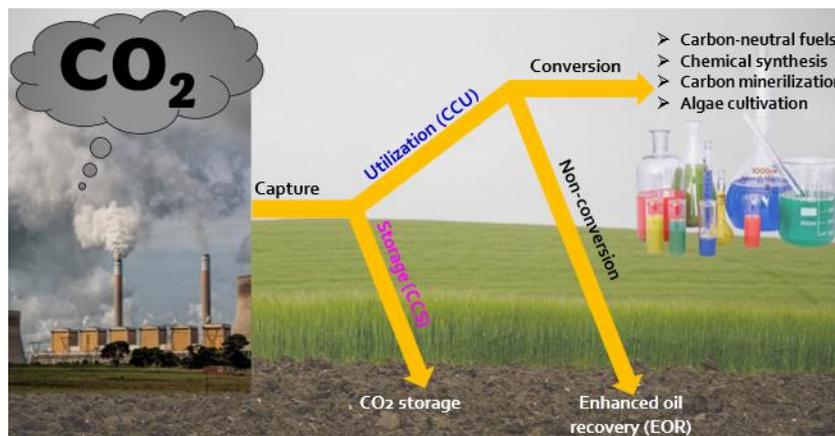


Figure 1. Concept of carbon capture and storage (CCS) and carbon capture and utilisation (CCU)

Dimethyl ether (DME, CH₃-O-CH₃) is an environmentally friendly, non-toxic oxygenate with intriguing properties that has a variety of applications. It is considered as a clean transportation fuel because of its high cetane number (55- 60), low boiling point (-25 °C), low ignition temperature and good composition of oxygen content (35 wt. %), which facilitate faster vaporisation and better combustion quality [4]. However, DME possesses lower heating value (LHV) as compared to diesel (27.6 vs. 42.5 MJ/kg). But due to no carbon-carbon bond in the chemical structure of DME, excellent combustion characteristic can be obtained where no particulate matter (PM) is generated during the combustion process. DME has also been considered as liquefied petroleum gas (LPG) replacement as it has similar vapor pressure to LPG. Thus, it allows the use of current infrastructures for transportation and storage [5]. As DME can be stored in liquid phase under very low pressure (~0.5 MPa) similar to LPG for gasoline engines, this minimizes the modification required to the engine if DME is used [6]. In addition, DME also acts as an intermediate chemical for the production of widely useful chemicals such as ethyl acetate and dimethyl sulphate as well as petrochemicals such as light olefins, BTX aromatics.

DME is generally produced from synthesis gas (syngas), a mixture of carbon oxides (mostly CO) and H₂. The syngas can be obtained from a various type of raw materials including crude oil, natural gas, coal, biomass waste, methanol via catalytic reforming or gasification with steam, CO₂ or oxygen [1]. Recently, the use of CO₂ and H₂ as feedstocks for DME production has been greatly considered due to its availability and the fact that the cost is less affected by the changes of oil price as compared to when syngas is used. In this perspective, the synthesis of DME from CO₂ hydrogenation allows the recycling of CO₂, which can effectively close the carbon loop [2-4, 7, 8].

DME Production

On an industrial scale, DME is produced based on a well-established technology using methanol as feedstock. In the first step of this indirect route, methanol is generated from syngas and then converted to DME in a subsequent reactor. Recently, a combination of the two reactions using the same reactor, known as a direct process, has been proposed. In the one-step direct process, the intermediate methanol synthesis stage is removed by using a novel bifunctional catalyst that operates at similar operating condition as methanol synthesis. Consequently, this results in cost reduction as well as promising efficiency (Figure 2).

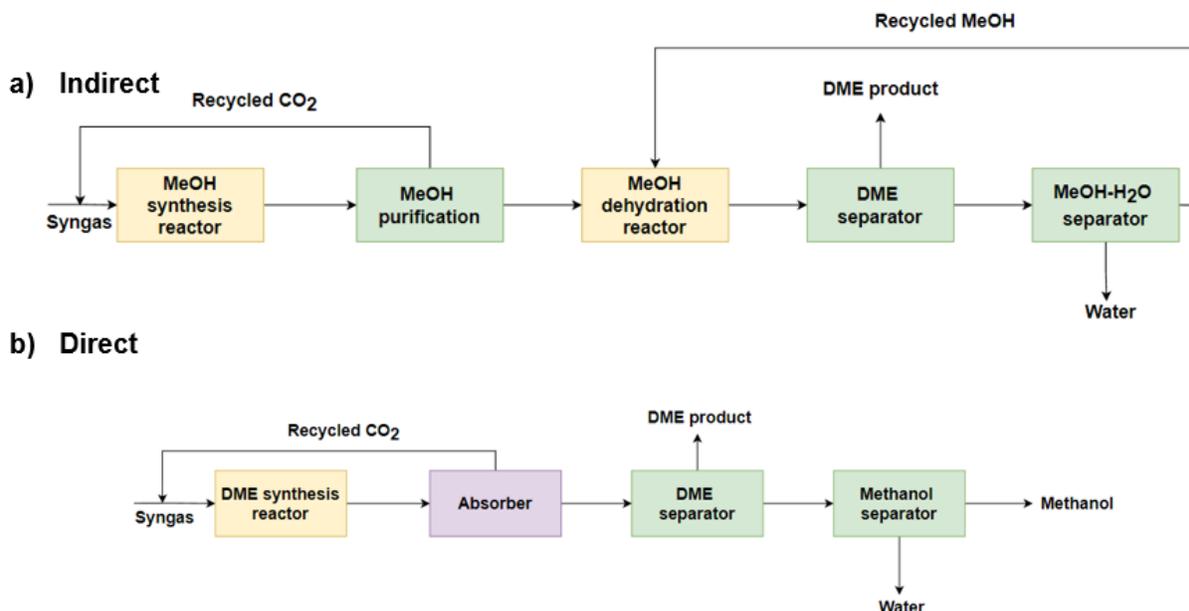
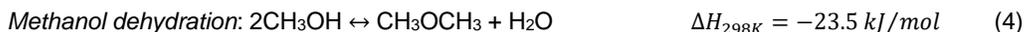


Figure 2. Schematic flow for (a) direct DME synthesis (b) indirect DME synthesis

Indirect synthesis involves a two-step process where the methanol synthesis and dehydration processes happen in separated reactors. The methanol synthesis takes place in the first reactor where syngas, H_2 will react with CO and CO_2 in the appearance of a copper-based catalyst according to the stoichiometric reaction (Eq (1) and Eq (2)) to form methanol. Due to the existence of H_2O in the second reaction, the water gas shift (WGS) reaction is also involved if CO_2 [9].



Many industrial plants such as Haldor Topsoe, Toyo Engineering (TEC), Oberon Fuels, BioDME and Lurgi (Air Products) produce DME through indirect approach. The main attraction for this process is the availability of the technology to obtain methanol and the simplicity of methanol dehydration. In addition, this approach allows the reactor for methanol dehydration process to be attached with the current methanol production facility for DME synthesis, when needed [10]. Based on Eq 1 and Eq 2, the CO and CO_2 hydrogenation processes are extremely reversible exothermic reaction where both kinetic and thermodynamic controlled. Therefore, the operating temperature needs to be properly maintained through efficient heat removal. From Figure 2 (a), it can be seen that after the production of methanol, it is purified using distillation columns where unreacted reactants are recycled back into the methanol reactor. The methanol stream is then directed to a dehydration reactor to produce DME. The dehydration of methanol to DME in the second reactor is facilitated by an acidic catalyst such as H^+ Zeolite Socony Mobil-5 (HZSM) or aluminum oxide (Al_2O_3). In this reactor, DME and water are produced in vapor phase [11]. The methanol/water/DME mixture is separated in a series of two distillation columns. The unreacted methanol can then be recycled back into the DME reactor after being separated from DME and water.

Recently, a direct synthesis of DME from syngas in a single reactor utilized bifunctional catalysts (Figure 2b). This type of catalyst possesses both metal active sites and acid sites for methanol synthesis and its subsequent dehydration, respectively. As both reactions are accomplished in one reactor, the needs for intermediary purification and transportation units can be eliminated, leading to more efficient process at lower operating cost. In addition, the thermodynamic constraints of methanol synthesis can be resolved by merging both processes in one reactor, which optimizes syngas conversion and DME selectivity [12].

When the feed is mainly syngas, the net reaction of DME production is based on Eq (5). However, the stoichiometry shifts to Eq (6) when CO_2 is used as feed or when there is a significant amount of CO_2 presents in the syngas, since the WGS equilibrium is suppressed. Starting from the progress made in

the CO₂ rich syngas-to-DME conversion, CO₂-to-DME production has been extensively investigated by researchers around the world to reevaluate CO₂ not as a waste, but as a valuable reactant. This strategy aims to contribute toward solving several critical challenges; the increasing demand of renewable fuels together with the need to substitute the fossil sources with raw materials of low or zero-carbon footprint, encouraging the research of alternative pathways to produce DME [13]. For this reason, there is a growing interest around DME production technologies based on CO₂ hydrogenation, where besides rich CO₂ syngas feedstock, pure CO₂ obtained from CO₂ capture system can also be used as a feedstock.



From the net reaction of direct CO₂ hydrogenation shown in Eq.6, a decrease in reaction temperature or an increase in reaction pressure should favor the synthesis of DME [14]. However, from a kinetic point of view, only an increase of reaction temperature above 220 °C facilitates the CO₂ activation rate. As a result, the formation of DME could be paralleled by the competitive formation of methanol (Eq. 2) and/or carbon monoxide (Eq. 3).

Challenges in the Direct Production of DME

Direct DME production from CO₂ is generally preferred at high pressure (40-60 bar) and lower temperature (200-280 °C) due to the decrease in the number of moles and to minimize endothermic side reactions such as RWGS that consumes CO₂ and H₂, respectively. The high reactor pressure is typically maintained via backpressure valve. In addition to that, the high production of water linked to the strongly competing RWGS also reduces the selectivity toward DME. Thus, this route presents new challenges and thus, extensive research work is vital to make the process feasible. The following sections discuss on several main challenges associated to the direct DME synthesis with CO₂ as one of the reactant gasses. Among those are i) the thermal management of the reactors, ii) the challenging catalyst design and iii) the thermodynamic and kinetic limitations in the presence of syngas rich in CO₂.

Thermal management

Since the reactions involved in direct production of DME are extremely exothermic, thermal management of reactor is essential. Exothermic condition means the system releases heat and the temperature of the system will increase. Since the process is thermodynamically restricted, it is essential to control the system's temperature. A hotspot or temperature runaway can lead to the sintering of a copper cluster on a zinc-alumina support, which deactivates the catalyst and generates undesirable hydrocarbons like olefin, paraffin, and aromatics [15], coke deposition [16] are formed at temperature above 300 °C. Thus, a proper reactor design is essential to control the reactor temperature.

Catalyst design

Direct DME synthesis needs a highly efficient bifunctional/dual catalyst that is capable to operate at similar conditions to methanol synthesis reaction. The bifunctional catalyst must comprise metal and acid sites for dehydrogenation of CO₂ to methanol and its subsequent dehydration, respectively (Figure 3(a)). To counteract the unfavourable thermodynamics of the CO₂ hydrogenation, the catalyst should be highly active at low temperatures. It must also be capable of reducing the generation of CO during hydrogenation by inhibiting the reverse water-gas shift (rWGS) reaction and not vulnerable to deactivation by water formed [17]. However, extreme acidity of catalyst should be avoided since it may create and catalyse secondary dehydration reactions that produce mainly carbon deposits and hydrocarbon.

To enhance the performances of bifunctional catalyst, proper control of the catalyst preparation is crucial to control the equilibrium and a correct distance between the methanol and acid synthesis sites in order to optimize their cooperation and avoid their possible detrimental interactions. The essential issue in the design of a DME catalyst is the enhancement of catalyst composition and the intimate contact between distinct catalyst components. An efficient bifunctional catalyst should possess right functions for the acid and metal sites together with a right balanced portion to allow intimate contact between the acid and metal sites [12]. The well-dispersed metal particles with high reducibility and significant numbers of low acidic sites are necessary to enhance the catalytic production of DME. Bifunctional catalysts are usually prepared by a number of approaches such as physically or mechanically mixing the methanol synthesis catalyst with the solid acid catalyst, co-precipitation and core-shell structure (Figure 2(b)).

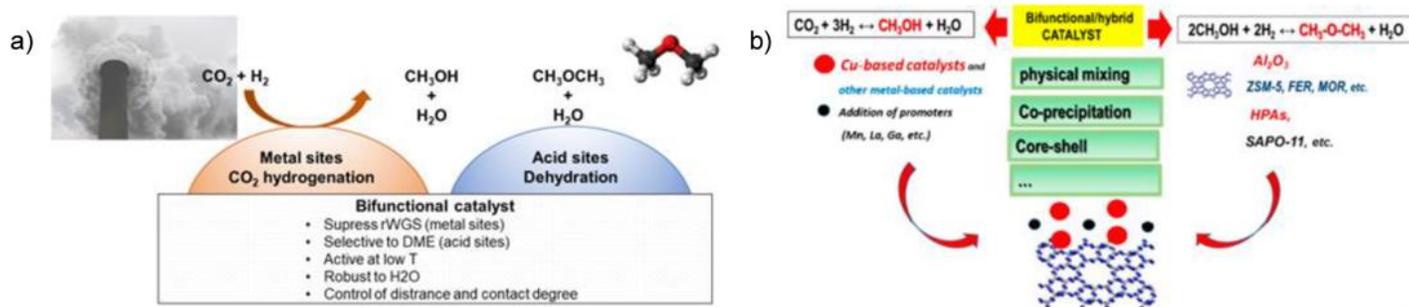


Figure 3. (a) Scheme of bifunctional catalysts and its requirements for the direct production of DME, and (b) general scheme to prepare the bifunctional catalyst for the direct production of DME [18]

The catalyst used for the methanol production from syngas is based on $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ (CZA), which operates in the range of 230–280 °C and 2–5 MPa. In comparison, $\gamma\text{-Al}_2\text{O}_3$ and zeolites are among the solid acid catalysts that have been widely investigated for methanol dehydration. Several works have indicated that a better efficiency could be achieved by combining $\gamma\text{-Al}_2\text{O}_3$ and copper-based catalyst. However, alumina-based catalyst has few disadvantages that lead to the low catalytic activities such as strong water adsorption and poor hydrothermal activity. A series of zeolites such as HZSM-5, silicoaluminophosphate (SAPO), mobil-type five (MFI) and H-ferrierite zeolite (H-FER) have been widely utilized as DME production catalysts due to its low temperature activity and high hydrothermal stability. Among those, the most widely employed for methanol dehydration catalyst is HZSM-5 since it has hydrophobic nature which is water resistant that leads to low catalyst deactivation.

Ren *et al.* [19] has investigated the effects of catalyst mixing method for the preparation of CZA and HZSM-5 bifunctional catalyst for DME production from CO_2 . Three mixing methods; method A-unpressed bifunctional catalyst (mixed by powders), method B-pressed then mixed and method C-mixed then pressed were compared. During the long-term testing, method B showed the best stability due to the reduction of Cu oxidation, which resulted from less surface contact between Cu active sites and HZSM-5. This indicated that that mixing method can significantly influenced catalyst stability. Polierer *et al.* [20] prepared $\text{Cu}/\text{ZnO}/\text{ZrO}_2$ using continuous co-precipitation method for DME production using $\text{CO}_2/\text{CO}/\text{H}_2$ feeds. It was found that the formed catalyst had high surface areas as well as improved metal dispersion due to faster and more homogeneous solid formation. Guffanti *et al.* [21] modelled a multi-tubular fixed-bed reactor, filled with several configuration of catalyst that mixed with hybrid pellets. The location of the catalyst is either coupled in core@shell-engineered pellets or in separated pellets. Different pattern distribution of the active phases was observed to have a great influence on reactor performance. Hybrid catalyst that possesses shorter diffusion length between methanol synthesis and dehydration catalysts has greater DME supply but higher hotspot temperatures, which could deactivate the catalyst due to the detrimental interaction between the two catalysts. $\text{MeOH}@$ DME was discovered to have a better DME production than the mechanical mixture and a lower hotspot temperature than the mixed pellet design. The core@shell catalysts have small diffusion distances and closed contact surfaces between the methanol and dehydration active phases.

Thermodynamics limitation

The thermodynamic limitations occurring in direct DME synthesis are evidently observed when a gas rich in CO_2 is fed to the reactor. This is due to the negative effect of H_2O , which is increasingly produced according to the stoichiometry in Eq. (6). The high concentration of water plays a significant role that can disrupt thermodynamic equilibrium of methanol synthesis and dehydration to DME, reduce the performances of the acid and metal sites of catalyst, deactivate the catalyst due to sintering in metal sites and formation of coke deposition. Dadgar *et al.* [22] observed that when the gas rich in CO_2 was fed to the reactor, the water produced increased which led to several issues of the catalyst such as deactivation of CZA methanol synthesis catalyst and water absorption of γ -alumina catalyst causing loss of its activity [5, 18]. Therefore, a possible solution to overcome this problem is by deploying in-situ water removal mechanism either by membrane or by in-situ adsorption. For the process scale-up, it is crucial to emphasize the importance of estimating the catalyst deactivation with kinetics while considering various factors and the related mechanism. In addition, the results of lengthy Time on Stream (TOS) should be thoroughly investigated to estimate the deactivation kinetics in order to develop accurate kinetic models.

Progress in the Reactor Development in DME Production

The establishment of direct synthesis of DME is very crucial on the reactor design strategies, where the synthesis of DME either from syngas or CO₂ exhibits extremely exothermic reaction and proper control of inner temperature of the reactor is essential to avoid the temperature runaway [23]. Many works have investigated the use of established types of reactors such as fixed bed reactor, fluidized bed reactor, slurry reactor, membrane reactor and micro reactor.

Fixed bed/Packed bed reactor

A fixed bed reactor (FBR) is often employed for pilot and laboratory studies due to its simplicity and low costs (Figure 4(a)). Owing to a simple flow pattern, a FBR is appropriate for a kinetic parameter study and many works have reported the kinetics of DME synthesis conducted in fixed bed reactors [24, 25]. For catalytic processes that have poor to moderate heat of reactions, the utilization of adiabatic fixed-bed reactor is favourable as it employs adequate longitudinal profile of temperature from the inlet to the outlet of the reactor [5]. Hot-spot mark usually formed at the inlet of reactor that favours the kinetic, while low temperature profile closer to the outlet of reactor helps to increase the equilibrium conversion [26]. However, this reactor is not appropriate for highly exothermic or endothermic reactions that result in catalyst sintering and some thermodynamic limitations. These issues may lead to reduced performance of catalyst and increase in syngas recycle rate to prevent rapid rise of temperature that might result in lower DME yield, large capital investment and increased operating costs. Thus, a proper reactor design is required to effectively remove the excessive reaction heat.

The relative velocity of the flow around the catalyst is favoured due to the heat transfer between phases in packed bed reactor. However, extra control is required to prevent any formation of hotspot and catalyst sintering because of the reaction conditions. To overcome the matters, heat transmission to the outside needs to be regulated. Then, to avoid radial temperature gradients, the diameter of the reactor is limited to L/D ratio of below 50. The heat transfer capacity can be increased using multi-tubular reactor systems (multiple tubes in parallel) as simulated by Pel'aez *et al.* [27] (Figure 4(b)). In order to further enhance temperature control, the isothermal packed bed reactor with external cooling was also proposed. The catalyst is positioned in a vertical tubes or shell surrounded by saturated water [28]. The heat from exothermic reaction is eliminated using saturated water and steam generated. After several studies, it showed that the isothermal reactor exhibited a better performance in terms of yield compared to the conventional fixed bed reactor. Alzate *et al.* [29] investigated the Lurgi-type reactor, which acts as a tube and shell heat exchanger, where the CuO-ZnO-Al₂O₃ catalyst was packed in the tubes and cooling water was circulated on the shell side to allow better process control. It was observed that the system had a great conversion by having efficient heat removal and weighted catalyst.

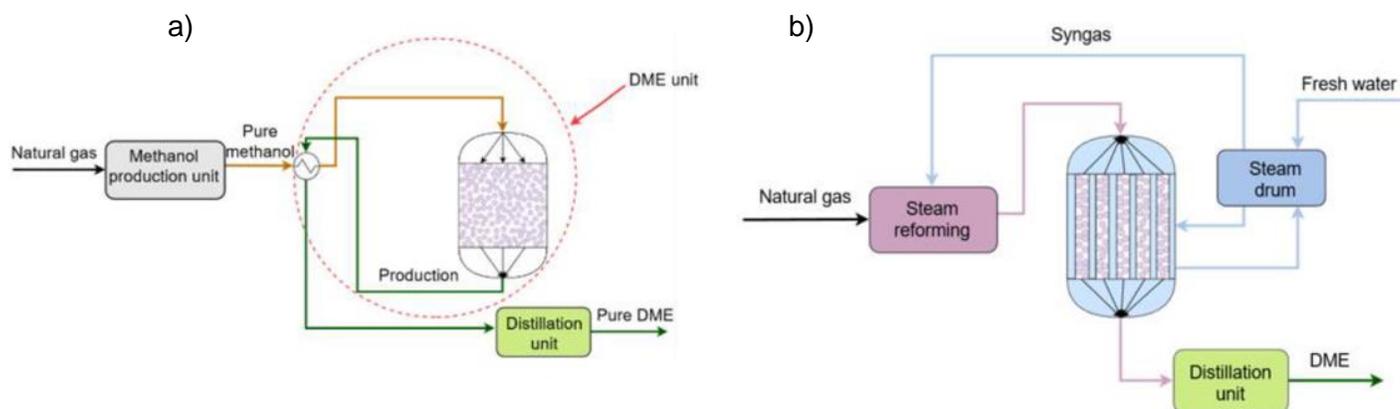


Figure 4. Schematic diagrams of (a) fixed bed reactor and (b) multi-tubular packed bed reactor [30]

Fluidized bed reactor

The improvement of reactor configuration for DME production leads to the design of fluidized-bed reactor (Figure 5). Fluidized bed reactor has been recommended for direct DME synthesis since it has excellent heat transfer performance owing to its turbulent mixing properties, rapid circulation mixing and freely moving catalyst particles in the bed. In this reactor, good temperature control is achieved due to the intense mixing of catalyst, reducing the gas–solid mass transfer resistance and preventing any hot spot formation during the reaction [31]. Other benefits of fluidized bed reactor include high conversion at

moderate operating pressure and without the need for recirculation [32]. However, catalyst lost might happen due to the collision between reactor wall and catalyst [33]. Currently, this reactor has only been tested at the initial state of laboratory scale and the applicability on large scale has not been done yet. Koyunoğlu *et al.* [34] reported a CFD simulation study to determine the conditions that provide maximum solid–gas contact in the zeolite catalyst bed of DME to be produced from syngas. It was observed that the catalyst density and the initial gas flow rate are important parameters that need to be controlled in order to provide maximum contact of the said gas flow to the catalyst surface.

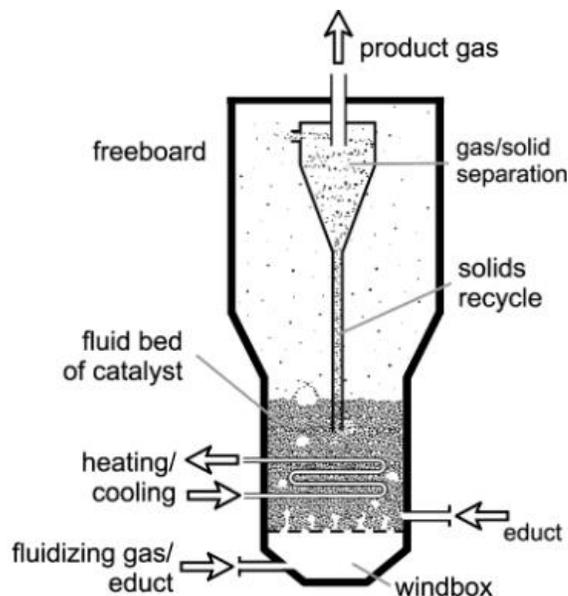


Figure 5. A schematic diagram of fluidized bed reactor [35]

Slurry reactor

Slurry reactor has received great attention among the researchers for the exothermic gas-liquid-solid reactions. This is due to several factors such as the simplicity of reactor's construction and the controllability of temperature profiles to avoid any hot spot formation [36]. It can be operated as a bubbling bed or continuous stirred-tank reactor (CSTR), where the gas reactant and solid catalyst will be in contact in a liquid medium. [37]. In a three-phase slurry reactor, syngas feed reactant is bubbled up as a third phase through a slurry in a reactor. This type of reactor is also capable to remove heat since it has high heat capacity of the liquid solvent and better performance of heat transferring from slurry to the heat exchanger tubes (Figure 6). Thus, the slurry reactor is allowed to operate in an isothermal condition during highly exothermic DME production [38]. Yagi *et al.* [39] studied the 100 tons/day of DME production that employed slurry phase reactor, where natural gas was the feedstock of the process and converted to synthesis gas by an autothermal reformer, ATR, which was then generated DME in slurry reactor. The disadvantage of this reactor is it has extreme limitations of mass transfer between phases due to the previous step of transferring the syngas in bubble states to liquid phase solvent, which lowers the overall reaction rate. A study by Naik *et al.* [40] found that the fixed bed reactor has better overall performances and catalyst stability as compared to slurry reactor due to the water accumulation on the catalyst surface. In addition to that, this type of reactor requires small particle size (<0.5 mm) of catalyst with high mechanical resistance [41]. It also involves complex equipment including catalyst separation unit to permit a recycling system, gas-liquid separator and continuous recirculation to the reactor.

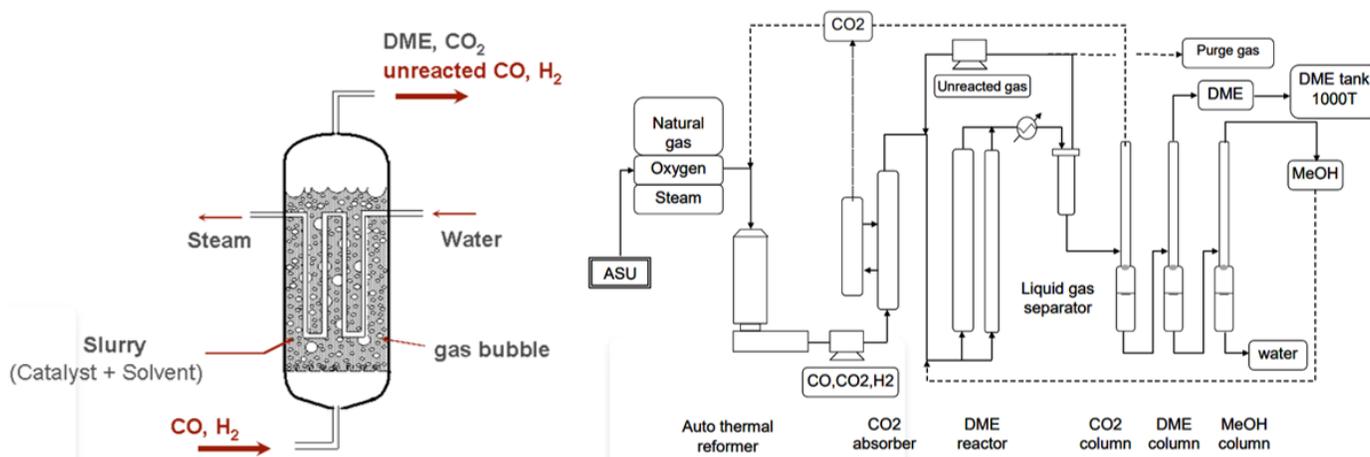


Figure 6. A schematic diagram of slurry reactor and process flow diagram, (PFD) of 100 tons/day of DME synthesis [42]

Coupled/dual-type reactor

DME synthesis involves reversible exothermic reactions. Therefore, choosing the appropriate temperature profile is essential as it may give impact on equilibrium conversion and reaction progress. As for the DME reaction, it is kinetically controlled at the beginning of the process and the reaction rate and conversion will increase eventually during the reaction progress. However, high temperature is not preferable as it might reduce the equilibrium conversion of the reaction. In order to have higher conversion during reversible exothermic reaction, the reaction needs to move towards the equilibrium by lowering the temperature profile [43]. A dual-type reactor arrangement, which consists of two reactors running under different conditions, can obtain the appropriate temperature profile for this reaction. Using the heat integration optimization idea, the heat produced by an exothermic reaction in this reactor is used as a heat source for additional endothermic reactions.

This reactor consists of two reactors which are water-cooled, and gas cooled, respectively. The bifunctional catalyst is filled in the tubes of first reactor (water-cooled) and subsequent reactor which is the shell side of the gas-cooled reactor, where the DME synthesis takes place (Figure 7)). The cold feed enters the subsequent reactor's tubes and is heated by reacting gas that is flowing in the reactor's shell side. The first reactor's tubes are fed with preheated syngas, and the DME chemical reaction is initiated over the packed catalysts. Exothermic reactions generate heat, which is absorbed by the boiling water on the first reactor's shell side and condensed into water vapour. The DME reaction is then continued at a lower temperature by admitting the outer reacting gas of the first reactor into the shell side of the subsequent reactor. The cold syngas and reacting gas streams flow in the next reactor in either co-current mode (parallel flow) or counter-current mode (in counter flow). While they flow in the same direction during co-current flow, the reacting gas stream moves in the opposite path to the synthesis gas stream during counter-current flow. Along the length of the reactor, the temperature of the reacting gas in a gas-cooled reactor drops, improving the equilibrium conversion. The product is then retrieved from the second reactors downstream. Vakili and Eslamloueyan [43] proposed this dual-type reactor made up of two fixed-bed reactors to get over reaction equilibrium's constraints. As fluidized-bed reactors have low mass transfer resistance, excellent heat removal characteristics, great thermal control, and high conversion, the dual-type reactor design has recently been developed [44].

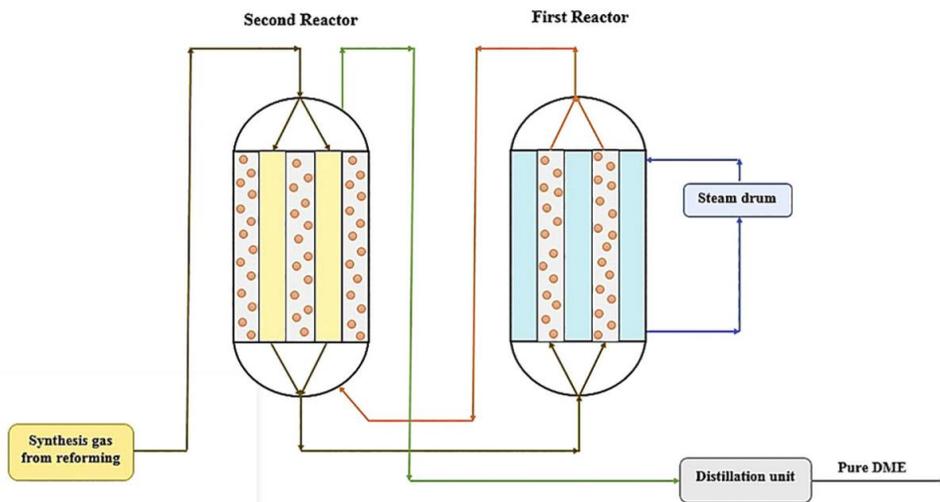


Figure 7. A schematic diagram of dual reactor [43]

Microreactor

Microreactor is a device where the chemical change takes place, having several parallel channels for liquids and gases with widths ranging from 10 to hundreds of micrometres. High surface-to-volume ratios and close proximity to the wall are made possible by the narrow channel dimensions, which facilitate heat and mass transfer (Figure 8). Due to quick diffusion in the tiny lateral dimension, gas phase reactions usually generate narrow residence time distributions.

The important stages of the microstructure reactor fabrication are the preparation of catalyst where the performance of the reactor is depending on the quality of coating obtained [45] and an excellent control during failed operation, leak or runaway [46]. Two variants of microchannel reactors for gas-solid heterogeneous reactions: catalytic bed and packed bed micro-reactors [47]. To generate DME from syngas, Hayer *et al.* [48] constructed a microchannel reactor with enhanced heat and mass transport. The results for experimental and simulation exhibited that the process was carried out in isothermal state in the microchannel reactor. If the attachment between the active phase and metallic substrate is low, a modification of the substrate, such as coating, should be performed [49]. Suspension features such as solid particle size, type of dispersing medium, solid concentration, and pH may have an effect on barrier qualities, and as a result, the effectiveness of the microreactor [50].

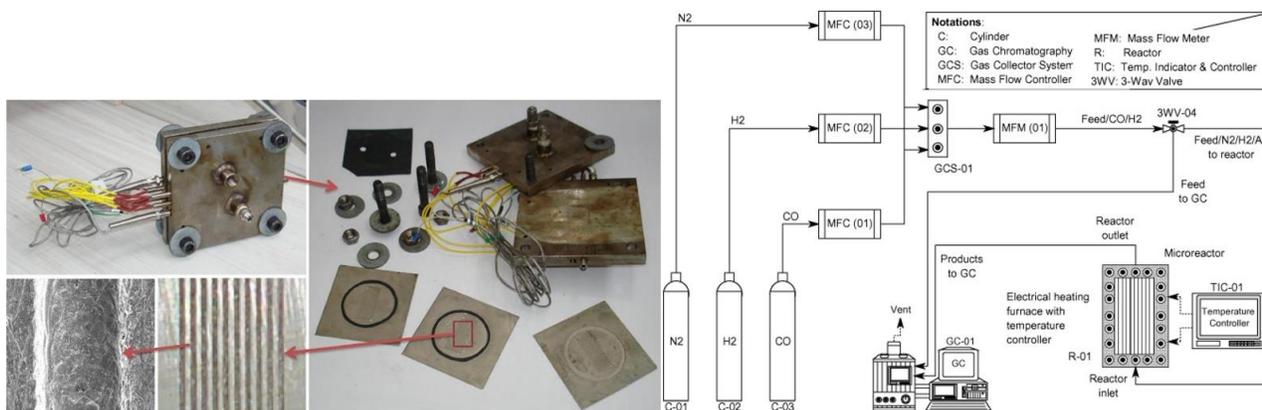


Figure 8. Microreactor for high pressure direct conversion to DME [49]

Membrane reactor

In direct synthesis of DME process, the existing H₂O limits the conversion of CO₂ and CO that results in low DME yield. Based on the Le Chatelier's principle, the reaction equilibrium can be shifted towards

selective DME, if the produced water is selectively detached from the system. Thus, the use of a hydrophilic membrane that favours the separation of H₂O from the reaction medium has received a great attention. By integrating the selective membrane in the catalytic reactor, the system is known as catalytic membrane reactor. Figure 9 shows the reactor configuration for catalytic membrane reactor where a H₂O permselective membrane is used to facilitate the removal of water with the assistance of sweep gas [9]. Generally, the location of membrane and catalyst are placed co-axially and in a packed bed, respectively. Conversely, the concentric tube with the membrane can be on either the outer or inner half of the catalytic bed. There are many available hydrophilic selective membranes depending on the materials and pore structure including polymeric membrane, amorphous microporous membrane and porous zeolite membrane. In general, the utilized hydrophilic membrane should possess excellent thermal stability at high temperature and operating pressure, great H₂O selectivity and high H₂O flux and stability. Looking into the operating conditions of DME synthesis, some of the membranes mentioned have issues with pore-blockage and thermal and mechanical stabilities. However, up until today, microporous zeolite membrane has been observed through a wide number of experimental and theoretical studies to be suitable for direct DME synthesis as it can withstand temperature above 200°C, possess satisfactory water molecule permeation of 10⁻⁷ – 10⁻⁶ mol·s⁻¹·m⁻²·Pa⁻¹ and has H₂O/H₂ selectivity more than 10 [51].

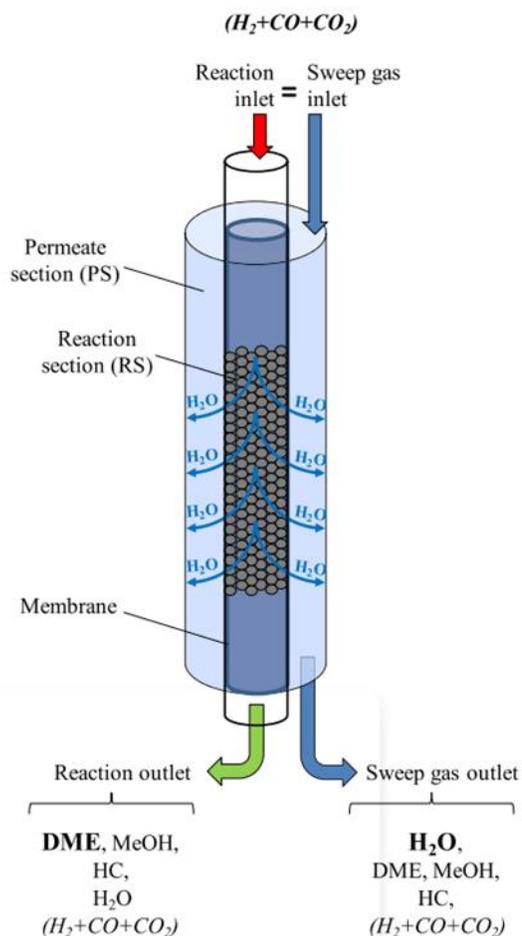


Figure 9. A schematic diagram of membrane reactor [52]

Table 1. Comparison of different types of reactor technologies from 2018-2023

Reactor type	Catalyst	Operating conditions	Overall performances	Conclusions	Ref
Fixed bed reactor	CZA – HZSM-5	T =210-270 °C P =20 – 50 bar H ₂ /CO ₂ =3:1 Space velocity =1000 – 10000 mL/(g.cat.h) L _{reactor} =0.5 m; D _{reactor} =0.012 m	X _{CO2} =30.9%; Y _{DME} =21.2%	The best operating temperature was less than 250 °C. The catalyst can deactivate above 250 °C due to sintering	[53]
Packed bed reactor	CuO-ZnO-ZrO ₂ @SAPO-11 core-shell catalyst	T =290 – 300 °C P =70 bar CO ₂ /CO _x =1	X _{CO2} =30%; Y _{DME} =32%	The use of SAPO-11 core-shell caused enhancement of yield due to the characteristic of core shell that allows to control complex reaction system involved including deactivation	[54]
Fixed bed reactors	CuO/ZnO/ZrO ₂ -ferrierite-type zeolite (CZZ-FER)	T =210-240 °C P=30 bar CO ₂ /CO _x =0.4–0.9 GHSV =0.4 s ⁻¹ Weight ratio CZZ/FER =1 to 70.4 L _{reactor} =600 mm; D _{reactor} =17.4 mm	X _{COX} =47%; S _{DME} = 88%	Lower GHSV increased CO _x conversion because the activity of the FER is less affected by water accumulation. Higher CO ₂ /CO _x leads to increasing of water formation. The use of FER enhances the performances due to flexible conversion of CO-rich and CO ₂ -rich syngas to DME.	[55]
Packed bed reactor	NA (simulation)	T=267 °C; P=40 bar	X _{CO2} =14.12%; S _{DME} = 59.3%	The recycling of unreacted H ₂ and CO ₂ caused enhancement of DME yield but additional compressor is needed	[1]
Stainless steel reactor	CZA – HZSM-5	T =250 °C; P =30 bar H ₂ /CO ₂ =2; GHSV =4800 h ⁻¹	X _{CO2} =41.8%; Y _{DME} =36.7%; S _{DME} = 64%	High conversion of CO ₂ to DME obtained from the combination of CZA – HZSM-5 using granule-mixing method due to the characteristics of hybrid catalyst that able to hinder coke deposition by water formation via methanol dehydration	[56]
Fixed bed micro reactor	CZA – HZSM-5	T =200 – 290°C; P =30 – 50 bar ; H ₂ /CO ₂ = 3 GHSV =2400 h ⁻¹	X _{CO2} =34.1%; Y _{DME} =23.1%;	The maximum temperature is 290°C and CO formation can be controlled up to that temperature due to the reducing number moles through methanol synthesis reaction	[57]
Microchannel reactor	CZA–HZSM-5	T =230 – 270 °C P=30 – 50 bar ; H ₂ /CO ₂ = 1 – 4 Space velocity =6000 mL/(g.cat.h)	X _{CO2} =73.3%; Y _{DME} =34.5%; S _{DME} = 47.07%	The CO ₂ conversion and DME yield increased by 59.75% and 54.2% when membrane was integrated due to responsiveness of the reactor to changes the temperature and pressure	[58]

Reactor type	Catalyst	Operating conditions	Overall performances	Conclusions	Ref
Fixed bed tubular reactor	CZA–HZSM-5	T =200 – 350 °C; P =30 bar H ₂ /CO ₂ =3 GHSV =48000 NL/h/kg _{cat}	X _{CO2} =2.1%; S _{DME} =77.5%	The S _{DME} was high due to strong Lewis's acid sites that catalyze DME formation. However, the X _{CO2} remained low since it has low Lewis acidity. DME formation mainly occurs in Lewis acid sites	[59]
Membrane reactor	CZA–HZSM-5	T=200 – 300 °C P =50 – 70 bar ; H ₂ /CO ₂ =1 – 3 GHSV = 6000 h ⁻¹	X _{CO2} =69%; Y _{DME} =75%; S _{DME} =99%	Temperature above 270°C gives negative effect on exothermal reactions and water steam permeation	[8]
Microchannel vs. cascade reactor (adiabatic packed-bed reactor & microchannel reactor)	CZA–HZSM-5	CO ₂ /CO _x =0.2 & H ₂ /CO _x =2.0, where CO _x =CO+CO ₂ = T =493°C P =50 bar RT =1.05 kgcat.s/mol	<i>Microreactor</i> X _{CO} =27.4%; X _{CO2} =6.6%; Y _{DME} =18.8% <i>Cascade</i> X _{CO} =23.3%; X _{CO2} =4.6%; Y _{DME} =13.8%;	Coolant inlet velocity has a dramatic effect on temperature & microchannel reactor performances. Pressure drop in microreactor is smaller than cascade reactor. The cascade system surpasses the thermodynamic constraints in terms of X _{CO} and Y _{DME} yield. But the X _{CO2} remains lower due to reaction kinetic	[60]
Membrane assisted reactor–microchannel heat exchanger	CZA–HZSM-5	T =250 P =50 bar CO ₂ /CO _x 0.7 H ₂ /CO _x =2	<i>With membrane</i> X _{CO} =58.9%; X _{CO2} =71.5% Y _{DME} = 56.9% <i>Without membrane</i> X _{CO} = 14.6%; X _{CO2} = 6.4% Y _{DME} = 10.3%	Incorporation of membrane with HEX improved the X _{CO2} conversion and Y _{DME} to 91% and 81.9% as it favors the kinetics and thermodynamics of syngas to DME conversion	[46]

**X denotes conversion, Y denotes Yield and S denotes selectivity

Future Prospect of Direct DME Synthesis

Dimethyl ether (DME) is an environmental-friendly fuel due to its high cetane number and clean-burning properties. The direct DME synthesis particularly using CO₂ as one of the reactants has received a worldwide attention due to its promising perspectives such as reducing CO₂ emission while producing valuable chemicals. Direct DME synthesis requires highly efficient bifunctional catalyst system that combines CO/CO₂ hydrogenation function for methanol synthesis and dehydration of methanol over acid catalysts to produce DME. The use of direct single-step synthesis is more energy efficient and might lead to the reduced capital and operating costs as compared to the two-step process via methanol synthesis and methanol dehydration. However, the main challenges in utilising CO₂ as a feedstock for direct DME synthesis are low reactivity of CO₂ hydrogenation and excessive formation of H₂O, which can result in the deactivation of catalysts. The existence of excessive H₂O in reaction compartment can cause the metal sites to absorb water, consequently, decrease the catalyst activity. In addition, the migration of active metal to the acid sites as well as to sintering is actively induced by the water being formed at the dehydration catalyst. To overcome the limitations, a study on the catalyst has been actively attempted by tailoring the conventional catalyst and proposing a new substitution that can favour the methanol synthesis and dehydration reactions together while lowering the catalyst deactivation. In addition, the contact between the active metallic and acidic phases should be minimized to reduce the water-induced sintering. As for further study, the development of a life-time catalyst to make the approach practicable and investigation on the efficiency of the catalyst in different types of reactors together with the mechanism of catalyst deactivation due to pore blockage and acid site coverage should be carried out.

Besides catalyst development, extensive research in reactor designs and its kinetic strategies have been done to enhance DME production using CO₂ as one of the reactants. For the past decade, varying types of reactors have been evaluated for DME production from syngas. A fixed bed reactor is widely recommended due to its design simplicity and operation system. However, the exothermic reactions and excessive H₂O formation increase the capital and operating cost of the reactor. As a result, many research works have focused on the development of small, clean and more energy-efficient reactor technology such as catalytic membrane reactor and microreactor. As the conventional reactor possesses the thermodynamic limitation of CO₂ conversion, different studies in in-situ adsorption of H₂O within the reactor were conducted. Their findings indicated that membrane reactor is one of the most potential reactors that can facilitate the DME production by improving the yield, conversion and selectivity. This is because the ability of membrane reactor to remove H₂O from reaction compartment using a hydrophilic membrane [61]. Although various researches have simulated the performances of these reactors, the experimental work on utilizing membrane reactor for practical application are still on-going especially in finding suitable materials that can withstand extreme condition of temperature and pressure during the DME synthesis. Table 2 summarizes the advantages and shortcomings of several reactors that have been investigated for direct synthesis of DME. Further studies are necessary to identify design solution for the direct synthesis of DME reactor. This includes providing maximum process intensity, heat recovery generated in the exothermic reaction, and conservation of catalyst performances, catalyst recovery and reusability.

Table 2. Characteristic of various reactors used for direct synthesis of DME from syngas

Reactor type	Operation	Advantages	Disadvantages
Fixed / packed bed (tubular)	<ul style="list-style-type: none"> Catalytic heterogeneous gas phase reaction. Reactions with low or intermediate heat generation are best suited. <p>Adiabatic fixed/packed bed</p> <ul style="list-style-type: none"> It is an isothermal reactor and the exothermal reaction can be carried out at the optimal temperature depending on the thermodynamics and kinetics of the reaction. Combination of a conventional reactor and heat exchanger. 	<ul style="list-style-type: none"> Simple design Low cost High mass and heat transfer rate between phases Easy to integrate external membranes (tubular) 	<ul style="list-style-type: none"> Large catalyst particle size (>1 mm) with diffusional limitations High pressure drop (lower in spherical reactor) Temperature profiles and hot spots for high conversion Gas recycling requirement for low conversion Difficulties for scaling up (using a multi-tubular reactor) Need to stop to replace deactivated catalyst and adsorbents
Fluidized	<ul style="list-style-type: none"> It is a special type of multiphase pneumatic contactor. 	<ul style="list-style-type: none"> Isothermal Operation in autothermic regime High mass and heat transfer rate between phases Ease of energy recovery Low pressure drop Catalyst circulation capacity Low residence time (high selectivity) Easy to scale up Easy to incorporate H₂O adsorbents 	<ul style="list-style-type: none"> Complex equipment to operate at high pressure Reduced catalyst particle size (<1 mm) High mechanical resistance of the catalyst required Fluid dynamic limitations (gas flow restrictions) Difficult integration of membranes to separate H₂O
Slurry	<ul style="list-style-type: none"> It is a special type of multiphase pneumatic contactor. 	<ul style="list-style-type: none"> Simple design Isothermal Operation in autothermic regime Catalyst circulation capacity Low pressure drop Ease of circulating H₂O adsorbents 	<ul style="list-style-type: none"> Reduced particle size (<0.5 mm) High mechanical resistance of the catalyst required Low mass and heat transfer rate between phases Limitations of internal diffusion in the catalyst Higher volume than the tubular (packed bed) reactor in the stirred slurry Catalyst separation required (with catalyst circulation) Difficult integration of membranes to separate H₂O

Reactor type	Operation	Advantages	Disadvantages
Dual type	<ul style="list-style-type: none"> Coupling of highly exothermic and endothermic reactions to intensify both the reactions. 	<ul style="list-style-type: none"> Reduced operation and production cost. Can be used as a process intensifier for many industries, highly energy efficient 	<ul style="list-style-type: none"> Difficult integration of membranes to separate H₂O
Micro	<ul style="list-style-type: none"> Used for the study of both exothermic and endothermic reactions. 	<ul style="list-style-type: none"> High mass transfer and heat transfer rates, high-risk reactions also can be operated; good control of the process 	<ul style="list-style-type: none"> Laminar flow of reactants inside the microchannels
Membrane	<ul style="list-style-type: none"> The hydrophilic water permeable membrane is added inside the reactor to continuously remove water molecules generated in the reactor from the direct and indirect method of DME synthesis 	<ul style="list-style-type: none"> Higher mass and heat transfer than the conventional reactors Easy to operate with different temperature regimes Low pressure drop Low residence time (high selectivity) Flexibility to optimize different objectives High performances 	<ul style="list-style-type: none"> Difficult design and control High cost of manufacture and operation Difficult to scale up Need to stop to replace the catalyst Difficult integration of H₂O separation strategies (adsorption or membranes)

A precise description of the performance of the DME synthesis process with the applied catalyst and in a wide range of operating conditions is very helpful for future scale up. The kinetic models developed combining those established in the literature for the synthesis of methanol and its dehydration, should offer good prediction of products yields in the direct DME production. Future work should include a kinetic study when pure CO₂ and H₂ are used as the reactants for the production of DME. Additionally, scaling up and refining the one-step synthesis of DME should be considered in the future work. Relatively few works have been performed on the leading role of CO₂ in DME synthesis, especially at the conditions of high space velocity. Despite the extensive number of works on DME production are available in literature, there are still limited study on the economic impact of the DME process from CO₂. The effects of reactant types including ideal CO/CO₂ ratio in the feed stream are still not well established in the literature and this is considered as a paramount factor in deciding the economic potential of DME production. However, the knowledge gained in the fundamental areas analyzed in this report opens up the possibility that the CO₂ to DME synthesis process could contribute to mitigating climate change.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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