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Hydrogenation of carbon dioxide (CO<sub>2</sub>) to fuels in microreactors: a review of set-ups and value-added chemicals production

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## 6 Hydrogenation of Carbon Dioxide (CO<sub>2</sub>) to Fuels in Microreactors: 7 A Review of Set-ups and Value-Added Chemicals Production

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9 Nikolaos D. Charisiou,<sup>d</sup> Alberto Villa,<sup>f</sup> Atul Bansode,<sup>g</sup> Gary Leeke<sup>h</sup>, George Manos,<sup>a</sup> and Achilleas  
10 Constantinou<sup>\*b</sup>

11 Climate change, greenhouse effect and fossil fuel extraction have gained a growing interest in research and industrial circles  
12 to provide alternative chemicals and fuel synthesis technologies. Carbon dioxide (CO<sub>2</sub>) hydrogenation to value-added  
13 chemicals using hydrogen (H<sub>2</sub>) from renewable power (solar, wind) offers a unique solution. From this aspect this review  
14 describes the various products, namely methane (CH<sub>4</sub>), methanol, ethanol, dimethyl ether (DME) and hydrocarbons (HCs)  
15 originating via CO<sub>2</sub> hydrogenation reaction. In addition, conventional reactor units for the CO<sub>2</sub> hydrogenation process are  
16 explained, as well as different types of microreactors with key pathways to determine catalyst activity and selectivity of the  
17 value-added chemicals. Finally, limitations between conventional units and microreactors and future directions for CO<sub>2</sub>  
18 hydrogenation are detailed and discussed. The benefits of such set-ups in providing platforms that could be utilized in the  
19 future for major scale-up and industrial operation are also emphasized.

### 20 Nomenclature

21	CCS;	Carbon capture and storage
22	CCU;	Carbon capture and utilization
23	CSTR;	Continuously stirred tank reactor
24	CO <sub>2</sub> ;	Carbon dioxide
25	H <sub>2</sub> ;	Hydrogen
26	CH <sub>4</sub> (C <sub>1</sub> );	Methane
27	CH <sub>2</sub> OH;	Methanol
28	C <sub>2</sub> H <sub>2</sub> OH;	Ethanol
29	DME;	Dimethyl ether
30	FT;	Fischer-Tropsch
31	RWGS;	Reverse water gas reaction
32	Ni;	Nickel
33	Cu;	Copper
34	Mo;	Molybdenum
35	Co;	Cobalt
36	Li;	Lithium
37	Na;	Sodium
38	K;	Potassium
39	Mn;	Manganese
40	Fe;	Iron
41	Ce;	Cerium
42	Rh;	Rhodium
43	Ir;	Iridium

44	Pt;	Platinum
45	Ru;	Ruthenium
46	In;	Indium
47	Pd;	Palladium
48	CeO <sub>2</sub> ;	Cerium oxide
49	MnO <sub>2</sub> ;	Manganese oxide
50	In <sub>2</sub> O <sub>3</sub> ;	Indium oxide
51	NiO;	Nickel
52	TiO <sub>2</sub> ;	Titanium oxide
53		
54	SiO <sub>2</sub> ;	Silicon dioxide
55	Fe <sub>2</sub> O <sub>3</sub> ;	Iron oxide
56	K <sub>2</sub> CO <sub>3</sub> ;	Potassium carbonate
57	NiCo;	Catalyst
58	ZnO;	Zinc oxide
59	Co <sub>3</sub> O <sub>4</sub> ;	Cerium oxide
60	ZrO <sub>2</sub> ;	Zirconium oxide
61	PdZn;	Catalyst
62	SBA-15;	mesoporous silica catalyst
63	ZrO <sub>2</sub> ;	Zirconium Dioxide
64	γ-Al <sub>2</sub> O <sub>3</sub> ;	gamma-alumina
65	P;	Pressure (bar)
66	T;	Temperature (°C)
67	H <sub>2</sub> O;	Water
68	s;	Second
69	h;	Hour
70	K;	Kelvin
71	mL;	Milliliter
72	m;	Meter
73	μm;	micro-meter
74	mm;	millimeter
75	cm <sup>3</sup> ;	Cubic centimeter
76	min;	Minute
77	DBT;	dibenzyltoluene
78	NPs;	Nanoparticles
79	Gt;	Gigatons

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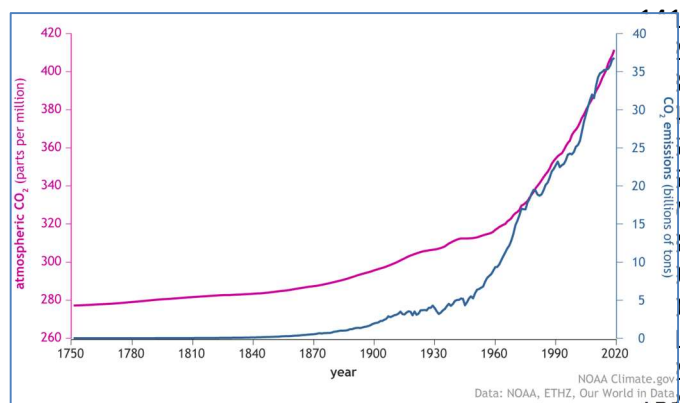
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## Introduction

Excessive extraction and utilization of fossil fuels combined with continuous greenhouse gas (GHGs) emissions have led to increasing carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere<sup>1</sup>. Recently, 33 Gt/year of CO<sub>2</sub> emissions were recorded, which contributes to a rapid increase in atmospheric carbon levels from 280 ppm to 410 ppm<sup>2</sup> when compared with preindustrial era. As a result of such conventional processes which utilise fossil fuels, the atmospheric CO<sub>2</sub> concentration is further predicted (Fig. 1) to increase to 570 ppm before the end of the century<sup>3</sup> if no CO<sub>2</sub> mitigation actions are taken. Two technologies: carbon capture and storage (CCS) and carbon capture and utilization (CCU) play a significant role in reducing CO<sub>2</sub> emissions<sup>4</sup>. Generating value added products through CO<sub>2</sub> hydrogenation utilising renewable hydrogen (H<sub>2</sub>), produced by water electrolysis<sup>5</sup>, has proven to be a major challenge in order to seek alternative fuel synthesis routes<sup>6</sup>.



**Figure 1.** Schematic showing the amount of CO<sub>2</sub> in the atmosphere (purple line) has increased along with human emissions (blue line) since the start of the Industrial Revolution in 1750<sup>7</sup>.

CCS is expected to play a vital role in limiting the GHG emissions, as well as climate change attenuation in the future. Specifically, it is considered an attractive alternative for the decarbonisation of emissions from industries and can also be merged with low carbon or carbon neutral bioenergy to produce negative emissions<sup>1</sup>. Whereas CCU attempts both the reduction of CO<sub>2</sub> emissions in the atmosphere and the substitution of conventional raw materials in distinct types of industrial processes through CO<sub>2</sub> hydrogenation. This method focuses on using carbon free viable technologies<sup>8</sup>. Renewable H<sub>2</sub> is generated through water electrolysis by applying electricity from renewable sources such as solar and wind and is widely used for the CO<sub>2</sub> hydrogenation processes<sup>9</sup>.

There are several carbon utilisation methods. CO<sub>2</sub> can be used as a feedstock for the production of fuels and chemicals. The main products derived from CO<sub>2</sub> are formic acid, urea, methanol, salicylic acid and cyclic carbonates. CO<sub>2</sub> is often converted into fuels or chemicals through biochemical, electrochemical, photochemical, thermo-catalytic, and hybrid methods. Industrial carbon emissions can be efficiently used via mineralisation processes to produce a range of products. The

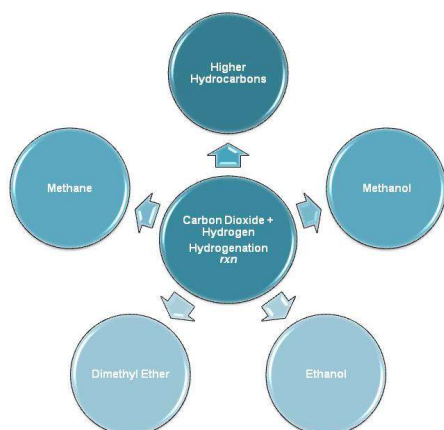
reaction is thermodynamically favourable, and a range of feedstocks (e.g., alkaline solid wastes and natural silicate ores) can be applied for the mineralisation processes. The mineralisation process can be divided into four main categories: direct and indirect carbonation, carbonation curing and electrochemical mineralisation<sup>10</sup>.

Potential of both conventional reactor units and microreactors in CO<sub>2</sub> hydrogenation has been demonstrated to obtain the chemical fuels. Conventional units such as continuously stirred tank reactors, fixed-bed reactors, fluidised-bed reactors (FBRs), packed-bed reactors and slurry reactors, have broadly been operational at industrial scale for the synthesis of value chemical fuels such as methane, methanol, ethanol, DME and higher hydrocarbons<sup>11</sup>, due to low cost and high heat and mass transfer<sup>12</sup>. Regardless of their applications, conventional units represent a high pressure drop, complex hydrodynamics and modelling<sup>11, 13</sup>.

The CO<sub>2</sub> hydrogenation process into hydrocarbons can be classified as two groups. This is the methanation reaction and the production of hydrocarbons through the Fischer-Tropsch (FT) process<sup>14</sup>. Consequently, CO<sub>2</sub> can be hydrogenated to methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), lower olefins, dimethyl ether (DME) and higher hydrocarbons<sup>15, 16</sup>. A scheme of the main products of CO<sub>2</sub> hydrogenation can be seen in Fig. 2. The production of olefins, i.e., ethylene and propylene, from the hydrogenation of CO<sub>2</sub> is a significant route. These olefins are the two most widely produced petrochemicals in the world. The worldwide ethylene and propylene consumption was nearly 150 million and 100 million metric tons, respectively. The demand for these chemicals signifies their imperative use in the chemical process industries as feedstocks and other materials, to produce solvents, plastics, polymers and cosmetics. Moreover, olefins can be further upgraded into long-chain hydrocarbons for use as fuels, rendering them as a high potential for using up to 23% of carbon emissions<sup>17</sup>. Generation of these chemical fuels was initially based on conventional reactor processes. However, many studies now are focused on the production of these fuels using microreactors, due to their potential in accelerating the generation of these value-added fuels<sup>18</sup>.

Great efforts have recently been accomplished to prepare microreactors with the aim of producing chemical fuels through CO<sub>2</sub> hydrogenation<sup>19</sup>. Microreactors such as continuous flow microreactors<sup>20, 21</sup>, micro packed-bed reactors<sup>22, 23</sup>, membrane<sup>24, 25</sup>, and microplasma reactors can be used to enhance various unit operations and reactions in micro space. Moreover, microreactors exhibit pivotal advancements in chemical engineering, leading to excellent output yield of chemical fuels<sup>26</sup>. Microreactors present high heat and mass transfer for highly exothermic reactions, while the dimensions of the microreactors components promote the enhancement of construction and operation.<sup>19, 27</sup> Finally, the microscale volume capacity of microreactors have also provided efficient progress of continuous flow reactions since they considerably decrease

the quantity of materials required to improve reaction conditions<sup>28</sup>. These reactors were used to synthesise chemical fuels for energy demand.



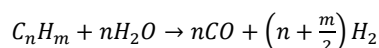
**Figure 2.** Schematic representation of carbon dioxide hydrogenation to value-added chemical fuels.

This review will provide a succinct illustration of the different routes performed to produce synthetic gases through CO<sub>2</sub> hydrogenation according to the challenges faced by conventional units and microreactors. The contribution of conventional units during CO<sub>2</sub> hydrogenation process will then be described. In addition, microreactors used to produce synthetic gases will be explained. Finally, limitations between conventional units and microreactors as well as future directions will be highlighted and discussed.

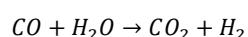
## CO<sub>2</sub> Hydrogenation to Value Added Chemicals Synthesis Routes

Hydrogen can be produced using various processes, Fig. 3 shows a brief overview of the many ways hydrogen can be obtained. Hydrogen required to react with CO<sub>2</sub> is conventionally produced from the steam reforming of non-renewable hydrocarbon feedstocks, and this has been the preferred industrial method for several decades.

Typically, the steam reforming process occurs via two reactions: (1) the steam reforming of the hydrocarbons, and (2) the water gas shift (WGS) reaction<sup>29</sup>.



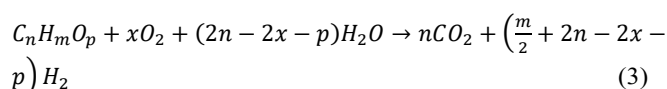
$$\text{for } n = 1, \Delta H^0_{298\text{ K}} = +206.2 \text{ kJ/mol}$$



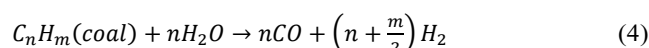
$$\Delta H^0_{298\text{ K}} = -41.2 \text{ kJ/mol}$$

Another conventional method for hydrogen production is autothermal reforming. This process is like the previously

described steam reforming; however, a proportion of the fuel reacts with oxygen to produce the thermal energy required in the reforming reaction which is an endothermic process. The generalised reaction for the autothermal reforming can be expressed as<sup>30</sup>:

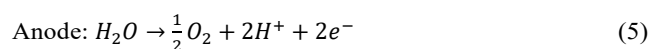


The value of  $x$  is related to the composition of the hydrocarbon. The gasification of coal is another significant reaction for the industrial production of hydrogen. The reaction products consist of syngas (CO and H<sub>2</sub>), and the CO can be further upgraded to H<sub>2</sub> and CO<sub>2</sub> via the WGS reaction. The primary reaction can be given by<sup>31</sup>:



Nonetheless, the coal gasification reaction is highly endothermic and requires reaction temperatures of 1273 K to acquire the desired product yield. On the other hand, the WGS reaction is exothermic and so lower reaction temperatures for the CO conversion are needed<sup>31</sup>. Typically, the coal gasification reaction is performed in a reactor with a temperature of 1273 K. The syngas product is then fed to another reactor which has a temperature below 673 K for the conversion of CO<sup>32</sup>.

The other approach is to produce the hydrogen from renewable energy sources. The electrolysis of water is one of the well-established methods to produce hydrogen as it utilises renewable and generates solely pure oxygen as a by-product. Furthermore, the electrolysis process is envisioned to use power from sustainable energy sources, such as wind, solar and biomass. However, currently, only 4% of the total hydrogen produced is coming from the electrolysis of water. This is mainly due to the economic issues<sup>33</sup>. The various electrolytes systems for the electrolysis of water can be represented by alkaline water electrolysis (AWE), proton exchange membranes (PEM), alkaline anion exchange membranes (AEMs), and solid oxide water electrolysis (SOE). The water electrolysis process can be represented by the following<sup>34</sup>:



The photocatalytic splitting of water with TiO<sub>2</sub> powders is the most basic configuration of the process, which is comprised of a sole type of semiconductor particles in continuous contact with water. Once excited by an incident photon with a greater energy than the bandgap of the semiconductor, an electron in the valence band can be pushed to the conduction band and generates a hole. Subsequently, the hole and electron separate specially and diffuse to the surface of the semiconductor to take part in the hydrogen evolution reaction and oxygen evolution reaction<sup>35</sup>.

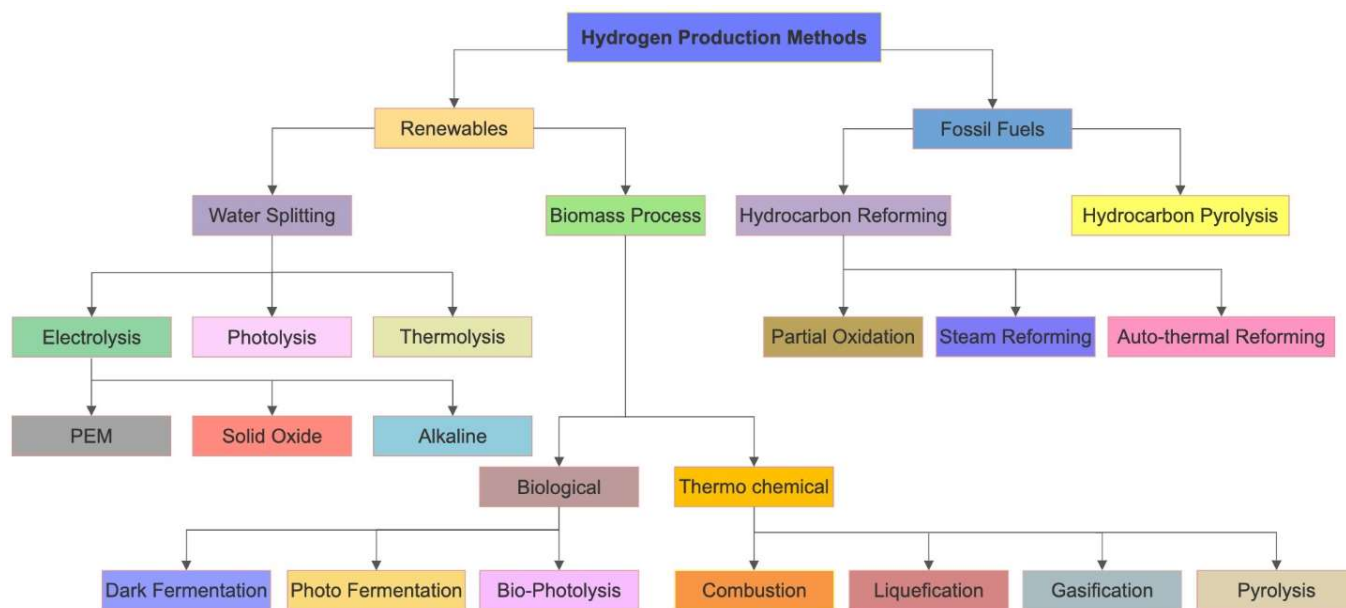


Figure 3. Overview of hydrogen production routes.

The hydrogenation process aids the reduction of atmospheric  $\text{CO}_2$  while producing fuels and value-added chemicals<sup>36</sup>. Hydrogenation to value added chemical fuels is considered a beneficial process, provided that renewable  $\text{H}_2$  is supplied<sup>37</sup>.  $\text{H}_2$  is a major utility that is typically produced from conventional petroleum reforming and could have major environmental implications. Remarkable advancements have been accomplished in the synthesis of  $\text{CH}_4$  ( $\text{C}_1$ ), methanol ( $\text{CH}_3\text{OH}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), dimethyl ether (DME) and higher hydrocarbons (HCs) directly from  $\text{CO}_2$  hydrogenation. Mixture of  $\text{CO}_2/\text{H}_2$  is required for the conversion into value added chemical fuels through the Fischer-Tropsch process and is often utilised widely in industry. Finally, synthesis of alcohols is more demanding than hydrocarbons by reason of accurate control of C-C coupling<sup>39</sup>. The resulting products of  $\text{CO}_2$  hydrogenation, such as hydrocarbons and methanol, are excellent alternative fuels for internal combustion engine with ease in storage and transportation. This alleviates many of the challenges associated with the use of fossil fuels<sup>36</sup>. Table 1 provides a summary of the main catalysts which are applied for the hydrogenation of  $\text{CO}_2$  into fuels and chemicals.

There are some issues which exist for the conversion of  $\text{CO}_2$  to value-added chemicals. Although the noble metal catalysts have a good performance, they are highly costly, and lack availability limits their wide scale applications for hydrogenation of  $\text{CO}_2$  to methane and ethanol. An alternative to this would be other metal catalysts, such as Ni; however, these catalysts are highly susceptible to deactivation due to sintering and carbon poisoning<sup>40</sup>. A similar issue exists with the  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst used for the hydrogenation of  $\text{CO}_2$  to methanol. A problem faced with this catalyst is the low selectivity towards methanol caused by the reverse water gas

shift (RWGS) reaction. Furthermore, the catalyst activity declines rapidly due to the water product, which leads to the sintering of the Cu component during the reaction<sup>41</sup>. The typical catalysts used for ethanol synthesis can suffer from the effects of high temperature, which promote the RWGS pathway and aids the production of undesirable  $\text{CO}$ <sup>42</sup>. Similarly, a prominent issue with the conversion of  $\text{CO}_2$  to higher hydrocarbons is the high selectivity towards methane and light saturated hydrocarbons<sup>43</sup>.

Table 1. Summary of catalysts applied for the conversion of  $\text{CO}_2$  into value-added chemicals.

Process Route	Catalytic System
Methane	Ru <sup>50, 58, 59</sup> , Rh <sup>60, 61</sup> , Pd <sup>62</sup> , Ni <sup>53, 63</sup> , and Co <sup>40, 64</sup>
Methanol	$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ <sup>60, 65, 66</sup>
Ethanol	Ru <sup>67</sup> , Pt <sup>68</sup> , Co <sup>69</sup> , Fe <sup>70</sup> and Cu <sup>71, 72</sup>
DME	Cu-based <sup>73-75</sup> , solid acid catalyst <sup>76, 77</sup> and zeolites <sup>78, 79</sup>
Higher Hydrocarbons	Fe <sup>80-82</sup>

### $\text{CO}_2$ to Methane

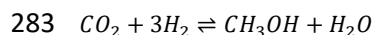
Methane ( $\text{C}_1$ ) is regarded a principal constituent of natural gases and can be successfully utilised in industry, energy and transportation sectors<sup>44, 45</sup>. The production of methane through  $\text{CO}_2$  hydrogenation is the most sustainable and convenient pathway to store significant quantities of energy generated from renewable sources<sup>46-54</sup>.  $\text{CO}_2$  hydrogenation to  $\text{C}_1$  reaction, initially revealed by the French chemist Paul Sabatier<sup>1, 55</sup>, can be represented as<sup>56, 57</sup>:



$$\Delta H_{298\text{K}} = -165 \text{ kJ mol}^{-1}$$

271 **CO<sub>2</sub> to Methanol**

272 Methanol is reported as one of the dominant chemical  
 273 materials in the chemical and petrochemical industry through  
 274 which methyl methacrylate, dimethyl carbonate,  
 275 chloromethane, acetic acid, formaldehyde, methylamine,  
 276 dimethyl terephthalate and methyl tertiary butyl ether  
 277 generated<sup>6</sup>. Methanol synthesis through CO<sub>2</sub> hydrogenation  
 278 has attracted tremendous interest as noble and oxide  
 279 supported metals have been regarded promising catalysts  
 280 controlling both the activity and selectivity of methanol<sup>60, 83</sup>.  
 281 Direct methanol (CH<sub>3</sub>OH) generation through  
 282 hydrogenation is represented as<sup>92, 93</sup>:



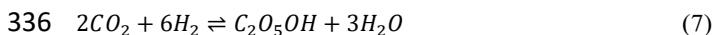
$$284 \Delta H_{298\text{K}} = -41.1 \text{ kJ mol}^{-1}$$

285  
 286 Remarkable progress has been made in CO<sub>2</sub> hydrogenation to  
 287 methanol and specifically in developing Cu and In-based  
 288 catalysts.<sup>94</sup> It is reported that over a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst  
 289 high CH<sub>3</sub>OH selectivity up to 98.2% can be accomplished under  
 290 conditions of P = 36 MPa and T = 220-300 °C<sup>95</sup> and a In<sub>2</sub>O<sub>3</sub>/ZnO  
 291 catalyst CH<sub>3</sub>OH selectivity can be up to 99.8% under conditions  
 292 of P = 5 MPa and T = 300 °C<sup>96</sup>. The remarkable selectivity and  
 293 conversion are due to the exceedingly high-pressure conditions  
 294 used for the study. Considering the catalytic kinetics for  
 295 methanol synthesis, development of highly effective noble  
 296 metal-based catalysts in terms of selectivity and stability  
 297 demanded<sup>97</sup>. Hartadi et al.<sup>98</sup> reported that over an Au-based  
 298 catalyst supported by TiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub>, high CH<sub>3</sub>OH  
 299 selectivity up to 82%<sup>97</sup> is accomplished under conditions of  
 300 5 bar and T = 220-240 °C. Malik et al.<sup>99</sup> have concluded that  
 301 over PdZn/CeO<sub>2</sub> and Ca-doped PdZn/CeO<sub>2</sub> catalysts, high CH<sub>3</sub>OH  
 302 selectivity of up to 100% is achieved under conditions of P = 35  
 303 bar and T = 220 °C.

304  
 305 Lee et al.<sup>49</sup> performed a techno-economic analysis for CO<sub>2</sub>  
 306 hydrogenation of CO<sub>2</sub>, and methane, to methanol. Three  
 307 processes were developed to investigate the production of  
 308 methanol from landfill gas. The first was a stand-alone process  
 309 (L2M-SA), and the second process had a hydrogen supply (L2M-  
 310 HS). The results from the techno-economic analysis showed  
 311 that the L2M-HS process has poorer economics, as opposed to  
 312 the stand-alone process, due to the excessive cost of hydrogen  
 313 supply. Furthermore, the unit production cost (UPC) of  
 314 the L2M-HS process was found to be around 12% higher than  
 315 the L2M-SA process. Nonetheless, the methanol produced from  
 316 the L2M-HS process can be economically viable with the current  
 317 methanol market if cheaper hydrogen supply routes are  
 318 available, e.g., using hydrogen which has been produced as a  
 319 product from industry. The study concluded that the UPC of  
 320 methanol is approximately 392-440 \$/tonne, which is  
 321 competitive with other conventional methanol production  
 322 processes. Furthermore, the lower environmental emissions  
 323 with the current process make it an environmentally cleaner  
 324 approach.

325 **CO<sub>2</sub> to Ethanol**

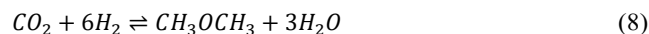
The conversion of CO<sub>2</sub> hydrogenation to high alcohols remains  
 an exceptional challenge due to the understanding of parallel  
 and successive reactions. Noble metals such as Au, Pt and Pd  
 are reported as catalysts for direct production of ethanol from  
 CO<sub>2</sub> hydrogenation with high selectivity up to 88.1% over a  
 Pt/CO<sub>3</sub>O<sub>4</sub> catalyst under conditions of P = 8 MPa and T = 220 °C.  
 Recent studies have shown that non-noble and metal-based  
 catalysts are investigated to provide highly efficient liquid phase  
 ethanol from CO<sub>2</sub> hydrogenation<sup>39, 69, 71, 100-106</sup>. Direct CO<sub>2</sub>  
 hydrogenation to ethanol is represented below<sup>107</sup>:



$$327 \Delta H_{298\text{K}} = -86.7 \text{ kJ mol}^{-1}$$

328 **CO<sub>2</sub> to DME**

DME is regarded as a significant chemical intermediate for the  
 generation of various chemicals such as diethyl sulphate,  
 methyl acetate, light olefines, and gasoline<sup>108</sup>. The  
 hydrogenation of CO<sub>2</sub> to DME has attracted great interest with  
 several heterogeneous catalysts<sup>74, 75, 77, 78, 109-112</sup>. Direct CO<sub>2</sub>  
 hydrogenation to DME is shown below:



$$330 \Delta H = -122.2 \text{ kJ mol}^{-1}$$

Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts and a mesoporous HZSM-5 zeolite are  
 used in DME synthesis, providing great resistance and  
 improving the mass transfer process during the reactions<sup>113</sup>.  
 Alvarez et al.<sup>114</sup> reported that direct CO<sub>2</sub> hydrogenation to DME  
 requires a bifunctional catalyst in order to perform methanol  
 synthesis and methanol dehydration. Utilisation of γ-Al<sub>2</sub>O<sub>3</sub> and  
 H-ZMS-5 catalysts<sup>115</sup> is investigated for direct conversion of  
 synthetic gas (syngas) to DME. Methanol synthesis can be a  
 physical mixture containing a methanol synthesis catalyst and a  
 solid catalyst which are mixed, and the function of the reactions  
 are divided. Methanol dehydration is considered an integrated  
 mixture where the catalytically active products of the reactions  
 are located to the nearest position so as to ease DME synthesis.  
<sup>114</sup>. Tokay et al.<sup>116</sup> investigated that over an Al@SBA-15 and  
 mesoporous AlSi<sub>3</sub> catalyst, high DME selectivity of up to 100% is  
 achieved under condition of T = 300-400 °C and a space time of  
 0.0027 s g/cm<sup>3</sup>.

Michailos et al.<sup>117</sup> investigated the production of DME from the  
 captured CO<sub>2</sub> hydrogenation within the context of power-to-  
 liquid context. The calculations were based upon a plant which  
 generates approximately 740 tonnes/day of DME. The results  
 from the economic analysis revealed that net production cost  
 of DME was 2112 €/tonne, and the minimum DME selling price  
 (MDSP) was 2193 €/tonne. The latter value is 5 times greater  
 than the average gate price of conventional diesel in 2016. This  
 high cost is mainly related to electricity price, due to the  
 electrolysis unit, as opposed to the parameters related to the  
 CO<sub>2</sub> capture and conversion plants. A subsidised or free of  
 charge electricity supply will make the DME price more



competitive; although, this will be unlikely due to the establishment of other technological options.

### CO<sub>2</sub> to Higher Hydrocarbons

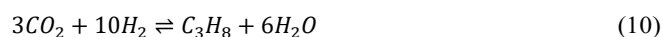
Higher hydrocarbons, such as light olefins and particularly ethylene and propylene generation, has gained great interest in the petrochemical industry<sup>118</sup>. Direct CO<sub>2</sub> hydrogenation to higher hydrocarbons is described as the combination of conversion CO<sub>2</sub> through the FT process and reverse water gas shift (RWGS) reaction.

The typical catalysts applied for the process are Fe-based due to their ability to catalyse both reactions. They can be utilised in bulk form or as supported iron oxides. In order to diminish the selectivity towards methane, the catalysts are doped with oxides of Cu, K, Mn, and/or Ce<sup>119</sup>. The most encouraging catalysts for this process are K promoted Fe/Al<sub>2</sub>O<sub>3</sub> catalysts with K contents of up to 0.5 mol-K mol<sup>-1</sup> of Fe. Nonetheless, these catalysts experience low efficiencies for the hydrogenation of CO<sub>2</sub>. This remains a major challenge for the production of higher hydrocarbons<sup>120</sup>. Recent studies have proven that CO<sub>2</sub> hydrogenation to value added chemical fuels can be realised by using the main catalysts for CO<sub>2</sub> hydrogenation with zeolites<sup>19</sup>.

CO<sub>2</sub> hydrogenation to higher hydrocarbons can be described below:



$$\Delta H_{298\text{K}} = -132.1 \text{ kJ mol}^{-1}$$



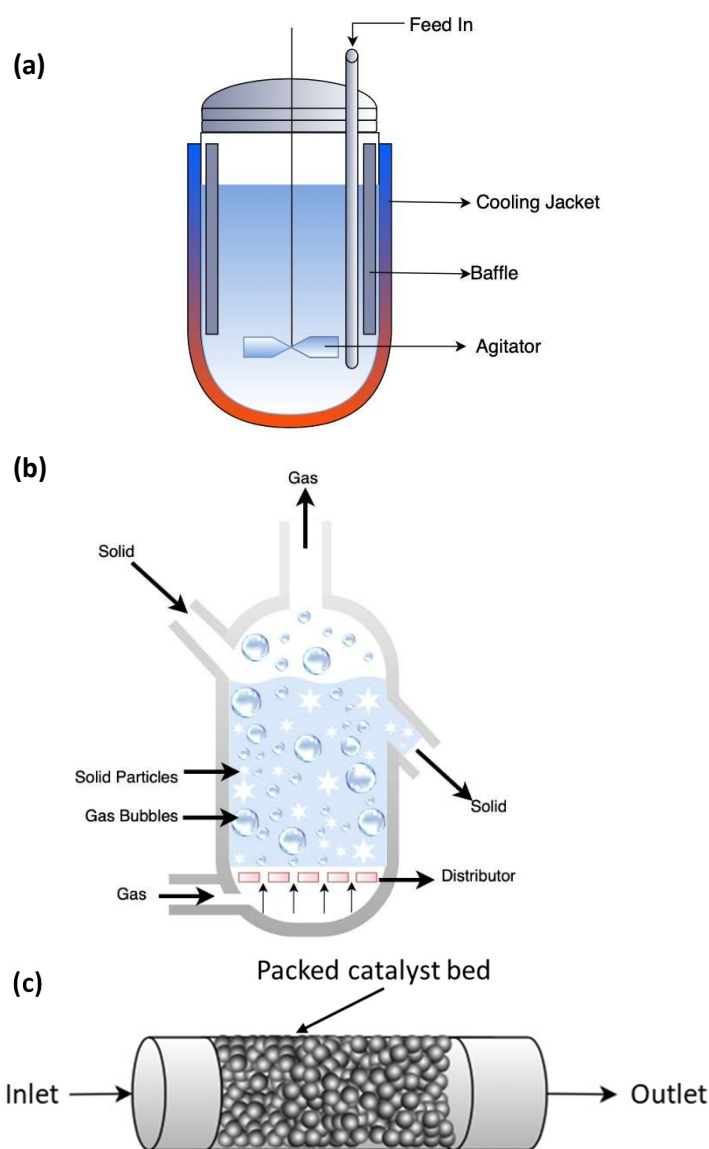
$$\Delta H_{298\text{K}} = -125 \text{ kJ mol}^{-1}$$

### Conventional Reactors in CO<sub>2</sub> Hydrogenation

The most used conventional reactors for the hydrogenation of CO<sub>2</sub> are continuously stirred tank reactors (CSTRs), fluidised bed reactors (FBRs) and fixed bed reactors. Fig. 4 shows a schematic of these conventional reactors.

#### Continuously Stirred Tank Reactor (CSTR)

CSTRs are considered as the most conventional reactors in the field of CO<sub>2</sub> hydrogenation. One of the operational issues with CSTRs is complex non-linear behaviour. These characteristics depict the requirement of a complex control system design. The results obtained from this non-linear analysis are significant as it allows the determination of difficult operating points, in order to remove them. As an example, it may be useful to operate around an unstable operating point, which can result in observation of higher product yields<sup>121</sup>. Nonetheless, CSTRs can provide wide operating range, as they can operate under steady state with continuous flow of both reactants and products. Fig. 5 shows a schematic of the CSTR process of the hydrogenation of CO<sub>2</sub> to produce methane. Chiavassa et al.<sup>122</sup> employed a Berty-type CSTR reactor for methanol synthesis

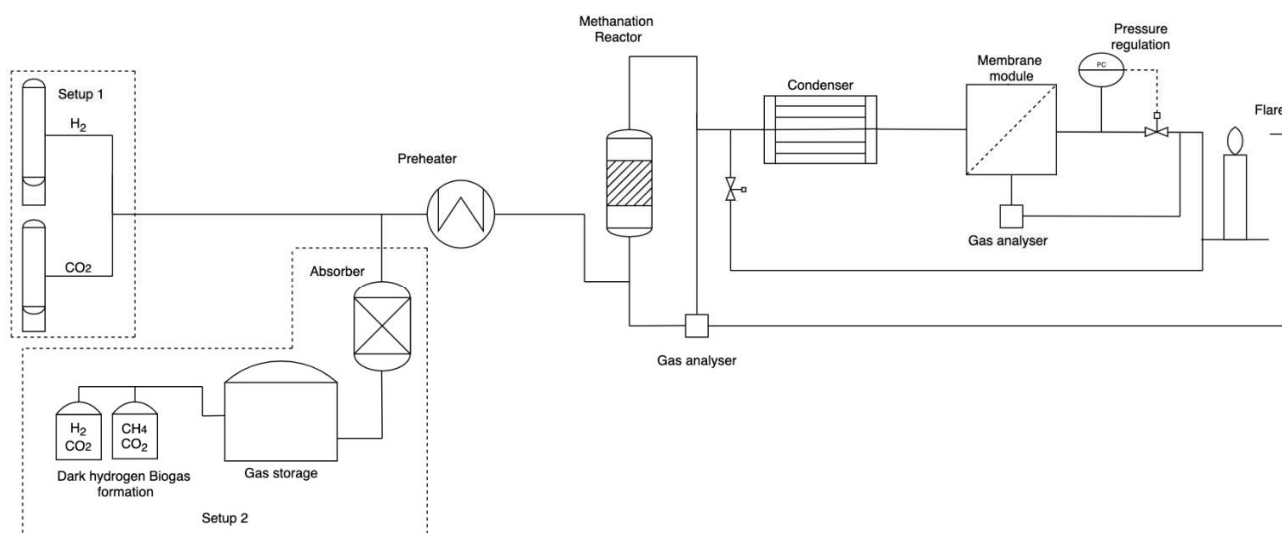


**Figure 4.** Schematic representation of the conventional reactors used commonly for the hydrogenation of CO<sub>2</sub>. (a) CSTR; (b) FBR; and (c) Fixed bed reactor.

through CO<sub>2</sub>/H<sub>2</sub> over Ga<sub>2</sub>O<sub>3</sub>-Pd/SiO<sub>2</sub> catalysts. The results showed that under conditions of P = 1-4 MPa and T = 508-523 K, CO<sub>2</sub> conversion to CH<sub>3</sub>OH was up to 70% and selectivity of CH<sub>3</sub>OH up to 50-55% was achieved.

Dorner et al.<sup>124</sup> used a CSTR for C<sub>1</sub> and C<sub>2</sub>-C<sub>5</sub> higher hydrocarbons synthesis, using Mn/Fe and K/Mn/Fe catalysts. Hydrogenation of CO<sub>2</sub> was accomplished under conditions of P = 13.6 atm, T = 563 K and gas hourly space velocity (GHSV) of 0.015 L/g s. The results showed that over Mn/Fe and K/Mn/Fe catalysts, CO<sub>2</sub> conversion to methane was up to 34.4% and 41.4% and selectivity was up to 42% and 29.4%, respectively. In addition, for higher hydrocarbons synthesis, the results showed that over Mn/Fe and K/Mn/Fe catalysts, CO<sub>2</sub> conversion to C<sub>2</sub>-C<sub>5</sub> higher hydrocarbons was up to 41.4% and 37.7%, and the selectivity reached 62.4% and 55.3%, respectively.





**Figure 5.** Flow sheet of the connected processes for CO<sub>2</sub> hydrogenation to methane using a CSTR.

Lefebvre et al.<sup>125</sup> used a CSTR reactor to identify the study of the three-phase CO<sub>2</sub> methanation reaction, applying commercial Ni/SiO<sub>2</sub> catalyst, suspended in the liquid phase. Feed gases were heated in a preferred temperature between 220 °C and 320 °C and mixed in a tempered feed tank. results showed that under conditions of  $P = 1$  atm and  $T = 320$  °C, CO<sub>2</sub> conversion to methane could not increase further for an agitator speed above ca. 1000 L/min and selectivity during the process was up to 95%.

Kirchbacher et al.<sup>126</sup> also used a CSTR reactor to produce methane derived from the reaction of CO<sub>2</sub> and renewable H<sub>2</sub>, generated by water electrolysis. For methane synthesis through CO<sub>2</sub> hydrogenation, two main processes were achieved. Initially, a high H<sub>2</sub>/CO<sub>2</sub> ratio was applied to prevent thermal effects of the spherical catalyst Meth 134<sup>®</sup>, which provides a high conversion to CH<sub>4</sub> that is approximately 80%. Methanation process was conducted at three pressure levels of 6, 10, 14 bar and a GHSV of 3.000, 4.000, 5.000 and 6.000 h<sup>-1</sup> under conditions of  $T = 395$ – $425$  °C. Secondly, under semi-continuous conditions biogas and synthetic H<sub>2</sub> were employed to generate methane. The feed gas composition was investigated by pressure levels of 6, 8, 10, 12 and 14 bar. However, GHSV was limited to 4.000 h<sup>-1</sup>. Methane productivity reached a level of 85% v/v under condition of  $P = 14$  bar.

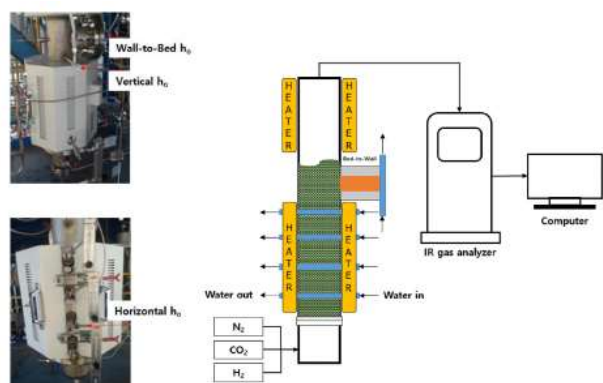
García-Trenco et al.<sup>127</sup> used a CSTR reactor to generate methanol through CO<sub>2</sub> hydrogenation, applying bimetallic Pd nanoparticles as catalysts. The results showed that Pd catalysts reduced methanol activity up to 50%, whereas catalyst including Pd/In intermetallic nanoparticles (Ni-Pd-In) exhibited high CH<sub>3</sub>OH rate up to 70% and high CH<sub>3</sub>OH selectivity up to 90%. Furthermore, the optimum Pd/In-based catalyst displayed an improvement in stability- the methanol production rate decreased by 20% after 120 h run, compared with 30% for the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (after 25 h).

A further study performed by García-Trenco et al.<sup>128</sup> investigated the hydrogenation of CO<sub>2</sub> to methanol using colloidal Pd<sub>2</sub>Ga-based catalysts in a CSTR reactor. The colloidal Pd<sub>2</sub>Ga-based catalysts shown 2-fold higher intrinsic activity than commercial Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> ( $60.3$  and  $37.2 \times 10^{-9}$  mol<sub>MeOH</sub> m<sup>-2</sup> s<sup>-1</sup>) and 4-fold higher on a Cu or Pd molar basis ( $3330$  and  $910$   $\mu$ mol mmol<sub>Pd or Cu</sub><sup>-1</sup> h<sup>-1</sup>) in liquid phase at a reaction pressure of 50 bar. The results showed a good correlation between the intrinsic activity and the content of Ga<sub>2</sub>O<sub>3</sub> surrounding the Pd<sub>2</sub>Ga nanoparticles (XPS), indicating that methanol is produced via a bifunctional mechanism concerning both phases. A steady decrease in methanol selectivity (60 to 40%) was observed when temperature was raised (190–240 °C) whilst an optimum methanol production rate was observed at 210 °C. Nonetheless, when compared to the conventional Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>, which suffered from around a 50% loss of activity over 25 h time on stream, the Pd<sub>2</sub>Ga-based catalysts sustained activity over this time frame.

In industry, it is common to utilise multifunctional metallic copper and zinc oxide catalyst on alumina (CZA). Huš et al.<sup>129</sup> investigated experimentally, and via multiscale modelling, of commercial-like catalyst (Zn<sub>3</sub>O<sub>3</sub>/Cu) and three other Cu/metal oxide combinations (Cr<sub>3</sub>O<sub>3</sub>/Cu, Fe<sub>3</sub>O<sub>3</sub>/Cu, and Mg<sub>3</sub>O<sub>3</sub>/Cu), synthesised by co-precipitation. The results showed that the formate species pathway (HCOO<sup>-</sup> → H<sub>2</sub>COO<sup>-</sup> → H<sub>2</sub>COOH → H<sub>2</sub>CO → H<sub>3</sub>CO) dominates on the studied Cu-based catalysts. Although, Zn<sub>3</sub>O<sub>3</sub>/Cu exhibited the highest conversion and a moderate CH<sub>3</sub>OH product selectivity, the former was smaller for Mg<sub>3</sub>O<sub>3</sub>/Cu. Furthermore, Cr<sub>3</sub>O<sub>3</sub>/Cu was ideal in terms of yield, but with exceptionally low CH<sub>3</sub>OH productivity, whereas Fe<sub>3</sub>O<sub>3</sub>/Cu functioned poorly overall.

## 499 Fluidised Bed Reactors (FBRs)

500 FBRs can be used for multiphase reactions due to the higher  
 501 heat and mass transfer and the efficient mixing among  
 502 reactants. Furthermore, FBRs are regarded as excellent in terms  
 503 of CO<sub>2</sub> hydrogenation to value chemical fuels, conversion  
 504 syngas, selectivity and economic feasibility<sup>4</sup>. Kim et al.<sup>130</sup> used  
 505 a FBR for direct hydrocarbon synthesis through  
 506 hydrogenation over K-promoted iron catalysts. A bench-scale  
 507 fluidised bed (inner diameter of 0.024 m and length of 0.6 m)  
 508 was applied for hydrocarbons synthesis. The results showed  
 509 that under conditions of pressure between 1 and 2.5 MPa and  
 510 temperature of 300 °C, CO<sub>2</sub> conversion to olefins was up to  
 511 46.8%, and olefins selectivity up to 89.3% was accomplished.  
 512  
 513 Nam et al.<sup>131</sup> used a bench-scale bubbling fluidised bed reactor  
 514 (shown in Fig. 6) for CO<sub>2</sub> hydrogenation to methane by applying  
 515 a Ni-based catalyst. Ni as a fluidising component and active  
 516 catalytic constituent was selected for use into a bubbling  
 517 fluidised bed reactor for CO<sub>2</sub> hydrogenation to methane.  
 518 bubbling fluidised reactor (diameter of 0.14 m and height of 1  
 519 m) was encircled by an electrical heater. The results showed  
 520 that a high CO<sub>2</sub> conversion to CH<sub>4</sub> up to 98% and CH<sub>4</sub> purity  
 521 to 81.6% was achieved, under conditions of temperature  
 522 between 280°C and 300°C and heat transfer ( $h_o$ ) of 115 W/m<sup>2</sup>.  
 523  
 524 Jia et al.<sup>132</sup> employed a fluidised bed reactor for direct  
 525 hydrogenation to methane, applied a Ni-Co based catalyst  
 526 supported on TiO<sub>2</sub>-coated SiO<sub>2</sub> spheres. A bench-scale fluidised  
 527 bed reactor was utilised for CO<sub>2</sub> methanation, consisted of a  
 528 quartz tube which was positioned in a tubular electric furnace  
 529 (inner diameter of 22 mm and length of 1 m). The results  
 530 showed that under conditions of ambient pressure and  
 531 temperature of 260 °C for over 120 h, CO<sub>2</sub> conversion to  
 532 methane was up to 52%, and CH<sub>4</sub> selectivity up to 97% was  
 533 achieved.



534 Figure 6. Bench scale fluidised bed reactor (left) and schematic diagram (right)<sup>131</sup>  
 535 (copyright permission obtained from Elsevier).

## 537 Fixed Bed Reactors

538 Fixed bed reactors are the most common type of reactor,  
 539 consisting of solid catalysts particles which are loaded and  
 540 packed in the bed<sup>133</sup>. In fixed bed reactors, gas, and liquid flow  
 541 below the catalyst bed from the top of the reactor to the

bottom, without stirring. Furthermore, CO<sub>2</sub> and H<sub>2</sub> are in direct  
 contact with the catalyst particles<sup>134</sup>. One of the major points  
 in fixed bed reactors is the temperature control in exothermic  
 reactions. The desired minimal CO<sub>2</sub> conversion can reach 90%.  
 Finally, the reaction time varies with the catalyst due to the  
 generation of H<sub>2</sub>O and the reaction rates<sup>135</sup>.

Ducamp et al.<sup>136</sup> used a cylindrical annular fixed bed reactor  
 (inner diameter of 20 mm, outer diameter of 50 mm and length  
 of 34 mm) to produce methane, by applying a commercial  
 catalyst made of a Ni active phase scattered on alumina trilobe  
 extrudates, and to analyse CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. The results showed  
 that under reaction conditions of pressure from 0.4 to 0.8 MPa  
 and a temperature between 200 °C and 275 °C, CO<sub>2</sub> conversion  
 to CH<sub>4</sub> was up to 85% and 89%, respectively.

Jaffar et al.<sup>137</sup> used a fixed bed reactor containing a gas  
 preheater to generate methane using a 10% wt. Ni-Al<sub>2</sub>O<sub>3</sub>  
 catalyst. The results showed that under condition of  
 temperature 360 °C methane yield up to 57.6% and methane  
 selectivity up to 98% was achieved. Kiewidt et al.<sup>138</sup> used a fixed  
 bed reactor to produce methane. A 5% wt Ru-based catalyst  
 supported by ZrO<sub>2</sub> loaded directly in the reactor with diluted  
 catalyst powder. The results showed that under reaction  
 conditions of pressure 10 bar and temperature 300 °C, methane  
 yield up to 90% was generated.

Castellani et al.<sup>139</sup> used a stainless mono tubular fixed bed  
 reactor CO<sub>2</sub> methanation. The results showed that under  
 reaction conditions of pressure from 2 to 20 bar and  
 temperature between 250 °C and 400 °C, methane conversion  
 of 31.36%, methane content up to 97.24% and CO<sub>2</sub> conversion  
 up to 99.6% was achieved. Willauer et al.<sup>134</sup> employed a fixed  
 bed reactor (shown in Fig. 7) (stainless steel tube) for direct  
 synthesis of hydrocarbons through CO<sub>2</sub> hydrogenation, using a  
 γ-Al<sub>2</sub>O<sub>3</sub> supported modified iron-based catalysts. The results  
 showed that under conditions of P = 265 psig and T = 300 °C,  
 CO<sub>2</sub> conversion of C<sub>2</sub>-C<sub>5</sub> hydrocarbons was up to 41.4% and  
 selectivity was up to 62.4%.

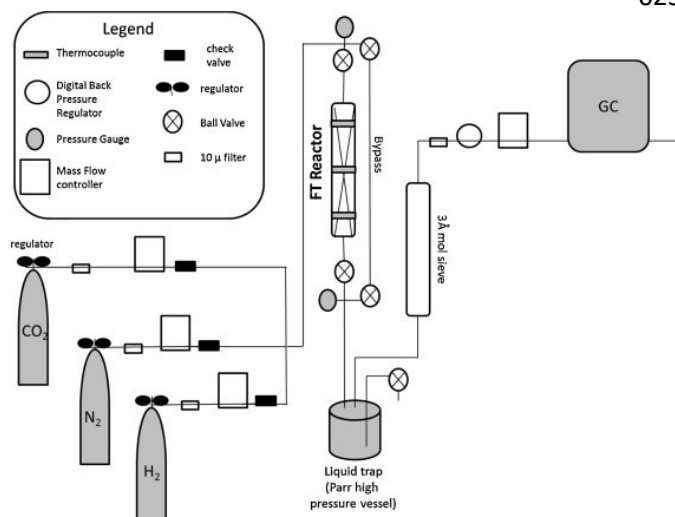


Figure 7. Flow sheet for CO<sub>2</sub> hydrogenation using a fixed bed reactor<sup>134</sup> (copyright permission obtained from Elsevier).

Pastor-Pérez et al.<sup>140</sup> used a fixed bed reactor for direct CO<sub>2</sub> hydrogenation to methane and applied Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts promoted with Mn and Co. CO<sub>2</sub> methanation process was conducted in a vertical continuous fixed bed quartz reactor (inner diameter of 10 mm), using 250 mg of the catalyst. The results showed that under conditions of T = 400 °C, CO<sub>2</sub> conversion to CH<sub>4</sub> up to 70% and CH<sub>4</sub> selectivity up to 99% was achieved. Furthermore, Bradley et al.<sup>141</sup> employed a fixed bed reactor to identify the role of the catalyst environment on CO<sub>2</sub> hydrogenation by applying a Macrolite® supported iron-based catalysts. The results showed that under conditions of T = 280–320 °C, CO<sub>2</sub> conversion to methane and C<sub>2</sub>-C<sub>5</sub> higher hydrocarbons up to 22–36%, CH<sub>4</sub> selectivity up to 26% and C<sub>2</sub>-C<sub>5</sub> higher hydrocarbons selectivity up to 60–69% were achieved.

Zhang et al.<sup>142</sup> investigated the selective hydrogenation of CO<sub>2</sub> and CO into olefins over sodium- and zinc-promoted iron carbide catalysts in a fixed bed reactor. The results showed that the selectivity of C<sub>2</sub>-C<sub>12</sub> olefins reached 78%, and the space-time yield of olefins attained as high as 3.4 g g<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> in CO<sub>2</sub> hydrogenation. Furthermore, the intrinsic formation rate of C<sub>2</sub>-C<sub>12</sub> olefins in CO hydrogenation was approximately twice higher when compared to that in CO<sub>2</sub> hydrogenation. The hydrogenation of CO<sub>2</sub> to olefins proceeds via CO intermediate over the developed catalyst.

Park et al.<sup>143</sup> studied the CO<sub>2</sub> hydrogenation to formic acid over heterogenised ruthenium catalysts using a fixed bed reactor with separation units. The results showed that the Ru/bpyTN-30-CTF catalyst prepared using the bpyTN-30-CTF support exhibits adequate catalytic activity for commercialisation. Under the continuous process, the catalyst displays considerable catalytic performance with the highest productivity of 669.0 g<sub>form</sub>.g<sub>cat</sub><sup>-1</sup> d<sup>-1</sup> with CO<sub>2</sub> conversion of 44.8% for a superficial gas velocity of 72 cm s<sup>-1</sup>. In addition,

catalyst shows excellent stability in the continuous hydrogenation process with a trickle-bed reactor over 30 days of operation, reaching a maximum turnover number of 524 000 devoid of any significant deactivation.

Bibi et al.<sup>144</sup> studied the hydrogenation of CO<sub>2</sub> using magnetic nanoparticles in a fixed bed reactor. The results showed that high activity and selectivity were obtained at 493 K, when MnFe<sub>2</sub>O<sub>4</sub> was calcined at 513 K (0.5 °C/min) for 4 h and reduced at 553 K for 2 h, while in the case of Bi-MnFe<sub>2</sub>O<sub>4</sub>, calcination was performed at 753 K (0.5 °C/min) for 6 h and reduced at 553 K for 2 h. It was concluded that a finger-projected fixed-bed reactor in combination with magnetic nanoparticles is a highly promising alternative for industrial conversion of CO<sub>2</sub> to MeOH to alleviate the effects of greenhouse gases.

## Microreactors for CO<sub>2</sub> Hydrogenation

Microreactors have been widely used to generate synthetic gases and liquid fuels from direct CO<sub>2</sub> hydrogenation, supported by reverse water gas shift reaction and Fischer-Tropsch (FT) process, in order to produce methane, methanol, ethanol, DME and hydrocarbons. The desirable characteristics of microreactors in the field of energy technology has attracted great attention in recent years. The benefits of microreactors, such as enhanced mass and heat transfer, shorter residence time and lower pressure drops, make microreactors an interesting option for gas conversion processes in which conversion and selectivity are closely linked to the mass and heat transfer properties of the reactor and catalyst<sup>145</sup>. In this section, the hydrogenation of CO<sub>2</sub> in packed bed and membrane microreactors, as well as microwave and microplasma reactors. Fig. 8 shows a schematic representation of the membrane and microplasma reactors.

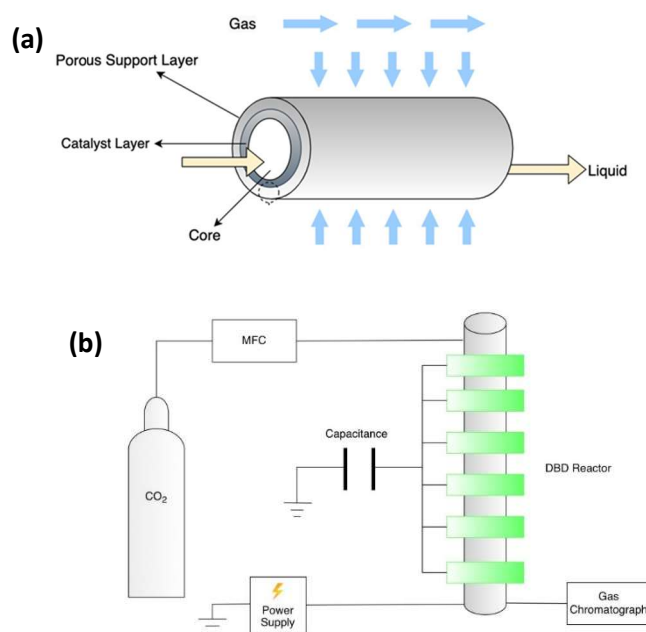
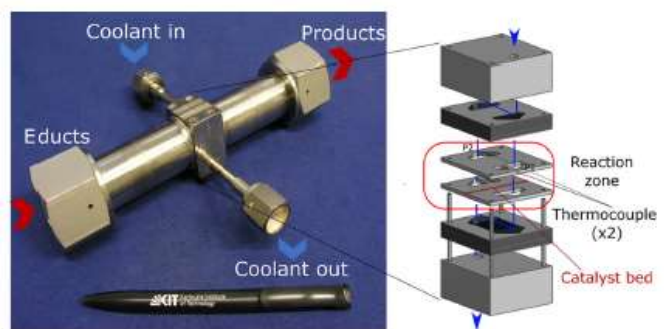


Figure 8. Schematic representation of (a) membrane microreactor; and (b) microwave reactor set-up.

## Packed Bed Microreactors

In packed bed microreactors, the heterogeneous catalyst is packed in a specific form into a microchannel. A packed bed microreactor provides easy loading and replacement of catalyst.<sup>146</sup> Farsi et al.<sup>147</sup> employed a microstructured packed bed reactor (shown in Fig. 9) with internal cross-flow cooling channel to investigate the kinetics of CO<sub>2</sub> hydrogenation to methane by applying a 17% wt Ni<sub>3</sub>Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The shorter bed length offered shorter contact time and prevented higher pressure drops. The results showed that the catalyst operated for over 120 min and under reaction conditions of 2 to 18 bar and 300 °C–450 °C, CO<sub>2</sub> conversion to CH<sub>4</sub> up to 92% and methane selectivity up to 99% was achieved. Kreitz et al.<sup>148</sup> used a microstructured fixed bed reactor to produce methane consisting of a 2 mm square channel. Spherical catalyst particles of 0.4 mm diameter were used to control the pressure drop and catalyst inventory. The results showed that under reaction conditions of pressure 8 bar and temperature 280 °C, a high CO<sub>2</sub> conversion of 97.8 % was accomplished.



**Figure 9.** Micro-structured packed-bed reactor<sup>147</sup> (copyright permission obtained from Elsevier).

Belimov et al.<sup>149</sup> used a microstructured packed bed reactor for the methanation process of CO/CO<sub>2</sub> mixtures by applying a commercial Ni-based catalyst to enhance the process. The results showed that after 2 h of the reaction and under reaction conditions of 200 °C to 900 °C, CO<sub>2</sub> conversion up to 95% and CH<sub>4</sub> selectivity up to 97% was achieved.

The hydrogenation of CO<sub>2</sub> to methanol has often been one of the most effective and economical methods of reducing the CO<sub>2</sub> emissions. Jiang et al.<sup>150</sup> studied the catalytic hydrogenation of CO<sub>2</sub> to methanol over Pd/In<sub>2</sub>O<sub>3</sub>/SBA-15 catalysts in a packed bed microreactor. It was found that the Pd/In<sub>2</sub>O<sub>3</sub>/SBA-15 catalysts exhibited superior catalytic activity with 83.2% methanol selectivity and 12.6% CO<sub>2</sub> conversion, corresponding to a STY of  $1.1 \times 10^{-2} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$  under reaction conditions of 260 °C, 5 MPa and  $15,000 \text{ cm}^3 \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ . Moreover, the authors found no apparent deactivation of the catalyst during the 120 h on stream, which implies a promising industrial application for the CO<sub>2</sub> hydrogenation for methanol synthesis.

Fang et al.<sup>151</sup> developed a hybrid catalyst/adsorbent consisting of Cu-ZnO-ZrO<sub>2</sub> supported on hydrotalcite (named CZZ@HT)

and performed the hydrogenation studies in a packed bed microreactor. The experimental results obtained using the packed bed microreactor demonstrated a methanol selectivity of 83.4% and a  $S_{\text{MeOH}}/S_{\text{CO}}$  ratio of 5 in products. A control experiment was performed by substituting the hydrotalcite in the previous catalyst, with quartz. It was revealed that significantly lower conversions at low pressures were observed for the quartz catalyst, thus depicting the desirable effect of the hydrotalcite support. Although the Cu-ZnO-ZrO<sub>2</sub> content in both catalysts was similar, the Cu surface area of the quartz catalyst was  $22.7 \text{ m}^2 \cdot \text{g}_{\text{catalyst}}^{-1}$ , as opposed to  $48.2 \text{ m}^2 \cdot \text{g}_{\text{catalyst}}^{-1}$  for the hydrotalcite catalyst. As a result, developed hydrotalcite catalyst could achieve the same methanol productivity as the control catalyst at 2.45 MPa which is a lower reaction pressure. This lower pressure corresponds to approximately 61.3% savings in energy consumption for compression.

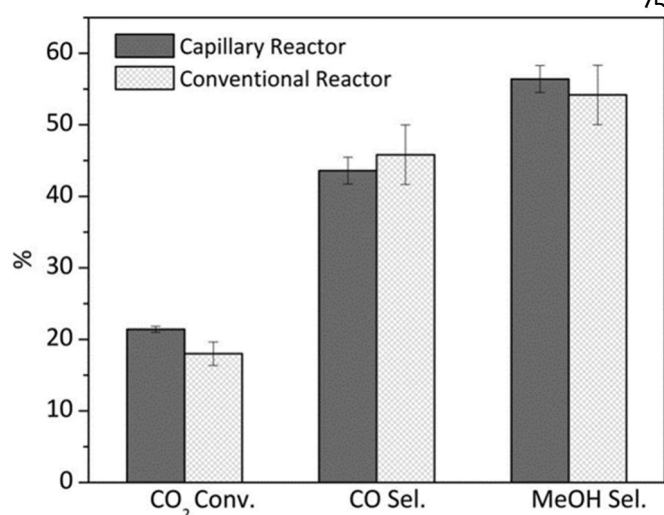
Koh et al.<sup>152</sup> investigated the structure-activity relationships of transition metal (Cr, Mn, Fe, Co, Ni) promoted copper-catalyst in direct CO<sub>2</sub> hydrogenation to methanol. The catalytic tests were performed in a continuous flow packed bed microreactor under kinetic controlled conditions. The results showed that at a reaction temperature of 180 °C, under reaction pressure of 4.0 MPa, WHSV of 60 L/gcat.h, and H<sub>2</sub>:CO<sub>2</sub> mole ratio of 3:1, the catalyst presented the highest methanol yield of 10.4%. The CO<sub>2</sub> conversion achieved was 10.5% and the methanol selectivity was 98.6%.

Koh et al.<sup>153</sup> synthesised a series copper-catalysts, Cu-ZnO-MnO (CZM), supported on morphologically distinct siliceous porous carriers (SBA-15, MCF, KIT-6) for the direct CO<sub>2</sub> hydrogenation to methanol. The catalytic tests were performed in a packed bed microreactor. The results showed that the KIT-6 supported catalyst (CZM/KIT-6) offered the most superior performance, this is due to the morphology of KIT-6 deterred mesopore plugging, favouring the formation of small copper crystallites. Furthermore, CZM/KIT-6 retained the greatest resistance to copper crystallite growth and loss of copper surface area during reaction due to the pore-confining effect of the porous carrier and the larger inter-crystallites spacing among copper crystallites. These advantageous catalytic properties provided the highest CO<sub>2</sub> conversion (8.2%) and highest methanol production rate ( $105.3 \text{ mol} \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ ) at low reaction temperature (180 °C). The methanol selectivity attained was  $\geq 99\%$  in all the experiments.

Liang et al.<sup>145</sup> investigated the hydrogenation of CO<sub>2</sub> to methanol using a Cu-Zn/Al foam monolithic catalyst in a packed bed microreactor. The reaction conditions used were 3 MPa and 250 °C at a high WHSV of  $20,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ . The results showed that the monolith catalyst generated a high methanol yield of  $7.81 \text{ g} \cdot \text{g}_{\text{Cu}}^{-1} \cdot \text{h}^{-1}$  and a 9.9% CO<sub>2</sub> conversion with a methanol selectivity of 82.7%. In addition, the porous aluminium pore substrate demonstrated a superior heat conductivity, and the monolithic catalyst does not change the nature of the reaction and maintains a uniform temperature distribution preventing hot spot formation.



The hydrogenation of CO<sub>2</sub> into methanol is an exothermic reaction and according to thermodynamics high pressure and lower temperature is beneficial to achieve high conversion of CO<sub>2</sub> into methanol. Typical CO<sub>2</sub> hydrogenation pressures are 5 to 10 MPa. Bansode et al.<sup>95</sup> exploited the advantages of high pressure for this reaction by performing the reactions up to 10 MPa in a microreactor to obtain almost complete conversion of CO<sub>2</sub> into methanol. Moreover, they also investigated the oxidation state of Cu in active catalyst under pressure of 20 MPa in a specially designed capillary microreactor. It was found that the Cu always remained in metallic state under the employed conditions of pressure and temperature<sup>154</sup>. In addition, the performance of such capillary microreactor was also elucidated and compared with conventional reactor system. As it can be seen in Fig. 10, almost identical catalytic activity was achieved in both reactors, detailing the advantage of capillary microreactor to use *in situ/operando* techniques which is normally not possible with conventional systems.



**Figure 10.** Catalytic performance in terms of CO<sub>2</sub> conversion and selectivity to CO and methanol (MeOH) in CO<sub>2</sub> hydrogenation using the capillary reactor and conventional microreactor<sup>154</sup> (copyright permission obtained from AIP).

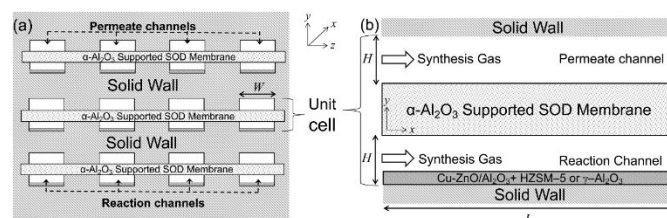
Tidona et al.<sup>155</sup> employed even higher pressures of 95 MPa in stainless steel microreactor. The study shown that the compression of CO<sub>2</sub> and H<sub>2</sub> accounts only for 26% of the total energy consumption whereas the main cost was associated with the hydrogen. This increase in pressure enhanced the space time yield by 15 times compared to literature reports.

Although packed bed microreactors have proved valuable for the hydrogenation of CO<sub>2</sub>, these reactors can suffer from high pressure drops when using small catalyst pellets. Furthermore, the use of solid catalyst particles can lead to plugging or fouling of the microchannels, leading to the obstruction of the continuous flow. To mitigate these effects, catalytically active metals can be used to cover the inside walls of the microreactor or can be placed on poles in the reactor channels, as seen in slug

flow microreactors and coated wall microreactors<sup>18</sup>. Furthermore, additional separation units are required to remove the desired product. Membrane microreactors offer a promising alternative due to the combination of reaction and separation zones into a single unit<sup>156, 157</sup>.

### Membrane Microreactors

A membrane microreactor combines the benefits of the microreactor and the membrane reactor, this leads to better intensified processes. The membrane microreactor is able to operate under milder reaction conditions because of higher mass and heat transfer and requires lower catalyst quantities when compared to other conventional reactors<sup>158</sup>. Koybasi et al.<sup>159</sup> investigated the hydrogenation of CO<sub>2</sub> to DME in a membrane microreactor (Fig. 11). The reactor is comprised of identical permeate and catalyst coated reaction channels, separated by an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported water-selective sodalite (SOD) membrane layer. The results showed that implementing the SOD membrane layer enhanced the CO<sub>2</sub> conversion from 7.2% to 12.4% and increased the DME yield from 12.7% to 15.3%. The reaction conditions used to achieve this were a pressure of 50 bar, temperature 523 K, a CO<sub>2</sub>/CO<sub>x</sub> ratio of 0.5 and a H<sub>2</sub>/CO<sub>x</sub> ratio of 2. Furthermore, increasing the temperature and pressure was found to enhance the production of DME. The performance of the membrane was heavily influenced by a CO<sub>2</sub>/CO<sub>x</sub> ratio in the range of 0.2–0.7. Lower ratios of 0.2 promoted the undesirable production of CO due to the reverse reaction. Increasing the inlet velocity of the syngas to the permeate channel promotes the membrane steam efflux and enhances the CO<sub>2</sub> conversion and DME yield.



**Figure 11.** Schematic representation of membrane microreactor used for the hydrogenation of CO<sub>2</sub><sup>159</sup> (copyright permission obtained from Elsevier).

Wang et al.<sup>160</sup> studied the hydrogenation of CO<sub>2</sub> to methanol using ZnO/t-ZrO<sub>2</sub> (ZrO<sub>2</sub> tetragonal phase) composite oxides in a membrane separation microreactor. The reaction conditions were a temperature of 320 °C, pressure 3 MPa, GHSV = 12,000 ml g<sup>-1</sup> h<sup>-1</sup> and a H<sub>2</sub>/CO<sub>2</sub> ratio of 3:1. It was found that different catalyst preparation techniques substantially altered the phase structure properties of the Zn/Zr hybrid interfaces and the CO<sub>2</sub> hydrogenation to methanol reaction. The microreaction synthesis technique had superior technical advantages due to the unique properties of the microchannels, such as an enhanced mixing efficiency and improved mass and heat transfer. The results showed that the solid solution produced from the microreaction demonstrated a superior catalyst

performance, temperature stability and catalyst regeneration. This was because of a highly constant solid solution structure, and rich oxygen vacancy defects. It was found that the CO<sub>2</sub> conversion, CH<sub>3</sub>OH selectivity, and methanol space time yield were 9.2 %, 93.1 %, and 0.35 g<sub>MeOH</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> respectively.

Despite the advantages membrane microreactors have offered for the hydrogenation of CO<sub>2</sub>, there are limitations which exist for this technology. For example, any alterations in the surface chemical and physical properties can influence the performance of the system which directly affects the surface tension, adsorption and electro-osmosis features substantially. Moreover, small particles in the fluid zone can cause blocking the microchannels in the reactor<sup>161</sup>. Microplasma reactors have become increasingly attractive due to their reduced power requirements, portability, and diminished power requirements. Furthermore, microplasmas provide a solution to the catalytic issues observed with the previously mentioned microreactors<sup>162</sup>.

### Microwave and Microplasma Reactors

The application of microwave technology in chemical processes is regarded well established in organic synthesis and materials processing. Microwave reactors can be efficient in CO<sub>2</sub> hydrogenation to value-added chemical fuels, using heterogeneous catalysts. Reactor design plays a major role both in modelling and fabrication in microwave technology<sup>163</sup>.

de la Fuente et al.<sup>164</sup> employed a non-equilibrium microwave plasma reactor for the reduction of CO<sub>2</sub> with H<sub>2</sub>. CO<sub>2</sub> hydrogenation was investigated in a non-thermal microwave discharge. A solid-state microwave generator with power of 100 W was applied to enhance the microwave energy to the plasma reactor. Plasma performed under pressure 7 to 200 mbar, while most of the reactants operated at pressure between 20 and 100 mbar. The results showed high CO<sub>2</sub> conversion to value-added chemical fuels up to 82%. Innovative microwave technology could be performed in order to define both conversion and selectivity for reactants and products under efficient control of temperature and pressure conditions<sup>165</sup>.

Chen et al.<sup>166</sup> studied the CO<sub>2</sub> hydrogenation in a microwave plasma reactor. The pulsed microwave plasma generation discharge took place in a quartz tube. An oil coolant is passed between the inner and outer tube. The results showed that the CO<sub>2</sub> conversion is significantly enhanced when the Ar plasma-activated NiO/TiO<sub>2</sub> catalyst has an NiO content is approximately 10 wt.%. Furthermore, the total CO<sub>2</sub> conversion fell from 28% to 14% for the pure CO<sub>2</sub> dissociation for a H<sub>2</sub>:CO<sub>2</sub> mixture ratio of 1:9. This was due to the presence of hydrogen lowering the temperature of the electrons and diminishing the vibrational effects of CO<sub>2</sub>. The hydrogenation of CO<sub>2</sub>, which occurred in a non-equilibrium microwave plasma reactor, reached a total conversion of 85% with an energy efficiency of approximately 6% and a CO<sub>2</sub> selectivity of 100%.

Wang et al.<sup>167</sup> performed the decomposition of pure CO<sub>2</sub> into CO and O<sub>2</sub> in a segmented electrode dielectric barrier discharge (DBD) microplasma reactor at ambient pressure. The results showed that a relatively higher CO<sub>2</sub> conversion and energy efficiency could be obtained at the propitious condition of longer interval between adjacent electrodes and smaller barrier thickness, and the highest CO<sub>2</sub> conversion and corresponding energy efficiencies are 16.9% and 3.6%, respectively, at the condition of an applied voltage of 18 kV and 1 mm barrier thickness. Furthermore, longer electrode intervals can lead to an increase in plasma density, as well as an enhanced fringe effect. Nonetheless, a smaller barrier thickness results in a smaller corresponding gas breakdown voltage, thus allowing more electrical power to be used for gas excitation. Therefore, more energetic electrons were generated and more collisions between the electrons and CO<sub>2</sub> molecules occurred. These factors are the main reasons for the enhanced CO<sub>2</sub> decomposition process.

Despite the promising applications of microplasma technology, there are some challenges which need to be overcome. Currently, the research is novel and limited. The technology suffers with issues in regard to system efficiencies, device lifetime and plasma consistencies. These plasma microreactors have experienced irregularities in plasma volume, power requirements, plasma stability, and plasma size and volume<sup>162</sup>.

### Limitations Between Conventional Units and Microreactors

Over the past decades, great progress has been made in conventional and microreactor technology, especially on the generation of value chemical fuels through CO<sub>2</sub> hydrogenation. One major question now rises whether microreactors can either complete with or replace conventional units in production procedures. To respond to this question, limitations between conventional units and microreactors will be described<sup>168</sup>. Table 2 provides a summary of the performance of both conventional reactors and microreactors.

A continuously stirred tank reactor performs in a dynamic state, which has some difficulties to control. This condition occurs when the values of the variables in a procedure are changing over time<sup>169</sup>. In fluidised bed reactors, due to high mechanical load resulting from fluidisation, attrition procedures occur in relation to the catalyst and the wall of the reactor. Consequently, the catalyst deactivates. Another major limitation can be the incomplete conversion caused by bubbling. A fluidised bed reactor is restricted by external gas velocity in the reactor, however, not too low to assure minimum fluidization, and not too high in order to prevent catalyst elutriation<sup>170-172</sup>.



**Table 2.** Summary of the advantages and disadvantages of microreactors and conventional reactors.

	<b>Microreactors</b>	<b>Conventional Reactors</b>
Mass and heat transfer	Often exhibit higher mass and heat transfer due to their characteristically smaller size.	Can sometimes suffer from mass and heat transfer resistances due to their larger size.
Pressure drops	Pressure drops are minimal in microreactor systems.	Higher pressure drops in larger packed bed reactors.
Production output	The numbering up of microreactors to increase their productivity to replace industrial reactors is currently limited.	The larger size of these reactors enables a larger production output for many chemical processes.
Environmentally friendly	The reaction conditions for some chemical processes in microreactors are milder (i.e., lower temperatures and pressures), making the processes more sustainable.	The reaction conditions for the same process are significantly higher, leading to a higher use of energy from fossil fuels.
Cost	Microreactors can sometimes be associated with high fabrication costs, and the numbering up of these devices can be expensive.	Conventional reactors are well established, so the construction of these units is cheaper.
Residence time	The small size of the microchannels significantly reduces the residence time, achieving high conversions with shorter times.	Some conventional reactors suffer from substantially longer residence times.

Fixed bed reactors are subject to high pressure drops. Moreover, these reactors tend to be more complex, while they exhibit higher costs<sup>173</sup>. Multiple fixed-bed reactors in parallel are demanded for larger plants. Preventing high pressure in reactor tube, large-scale catalyst particles are required, resulting in lower effectiveness factors (lower catalyst activity per unit mass, resulting from difficulties of reactants to scale in the core of the catalyst particle). Another major limitation of fixed-bed reactors face is lower heat transfer from the catalyst bed and the variation of temperature into the tubes. This fact results in a) difficulty in controlling the product composition, hot spots in the catalyst bed that may be led to both catalyst sintering and reactor instability, and c) lower conversions of 40% to prevent high temperatures (in that case unreacted feed can be recycled)<sup>174</sup>.

Microreaction technology is considered a field that has gained significant attention due to its great performance in operating processes compared to conventional units. Microreactors offer efficient manipulation of reactions, great response time, accurate control of environmental conditions, reduced consumption of both reagents and catalysts and also provide the opportunity of an integrated instrumentation, an in-line optimisation and automation methods<sup>175</sup>. However, microreactors exhibit major limitations, occurred by imperfections of microreaction technology during chemical processes. Highly fabrication cost, incompatibility over scaling and high economics of scaling up has led to inadequate industrial acceptance. Moreover, microreactors perform with shorter residence times, requiring the achievement of fast reactions. Fast reactions demand highly active catalysts, which should be stable in the microreactor. Consequently, microreactors cannot be applied as a replacement for classical processes yet<sup>176</sup>.

The comparison between conventional units and microreactors shows that higher heat and mass transfer can be accomplished by using a microreactor instead of a conventional unit, which exhibits lower bed hydrodynamics and temperature control. This characteristic is the main advantage for high exothermic reactions due to the great need of the reaction heat removal at a point where it is generated, resulting in a determined temperature profile over the reaction pathway. In addition, mixing can also be enhanced over a microreactor because of the reduced diffusion of mixing time to milliseconds<sup>27</sup>. Moreover, automated micro platforms have been reported in enabling design of experiments for optimization of operations conditions and reaction kinetics definition<sup>177</sup>. Microreactors system consisted of in-line and feedback control has been applied for the precision of operating conditions that can enhance a function for a reaction. It is significant to note that differences between microreactors and conventional units pose great challenges which require alternative prospects in order to be resolved<sup>175</sup>.

## Future Perspectives in CO<sub>2</sub> Hydrogenation

The hydrogenation of CO<sub>2</sub> is considered a sustainable procedure and a promising alternative for CO<sub>2</sub> utilisation. However, CO<sub>2</sub> is regarded chemically stable and thermodynamically unfavourable. High reaction heat, different types of reactors design and sensitive catalysts, indicates CO<sub>2</sub> hydrogenation to value-added chemical fuels (methane, methanol, ethanol, DME and higher hydrocarbons) a challenging procedure for further research and development.

For methane generation, catalysts containing noble metals such as Ru, Rh and Ir supported by  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  exhibit  $\text{CH}_4$  selectivity up to 100%, as regarded the most active metal. Ni-based catalysts such as  $\text{Ni/Ce}_{0.72}\text{Zr}_{0.28}\text{O}_2$ <sup>178</sup> and  $\text{Ni/MCM-41}$ <sup>179</sup> represent high  $\text{CH}_4$  selectivity up to 99% and 90% respectively. One of the crucial problems in Ni-based catalysts is considered the deactivation of the catalyst at high temperatures due the interaction of metal particles with  $\text{CO}$  formation of nickel subcarbonyls<sup>4</sup>. Consequently, this problem highlights the need for process optimisation in this field.

For methanol production, catalysts consisting of Cu represent a major role in improving methanol synthesis through hydrogenation of  $\text{CO}_2$ , with the most active catalyst component supported by  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ <sup>180, 181</sup>.  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst exhibits high  $\text{CH}_3\text{OH}$  selectivity up to 98%<sup>182</sup>. However, the bifunctional catalyst system poses major challenges for the application of a  $\text{Cu/ZnO}$ -based catalyst. It is considered a thermally unstable component and the size of crystallites can be increased at high temperatures, resulting in the loss of the active surface and Cu sintering<sup>73</sup>. Furthermore, Cu-based catalysts can be poisoned, and a lower lifetime may be occurred<sup>183</sup>. Consequently, this challenge should emphasise the need for further research, as well as catalyst regeneration.

For ethanol synthesis, noble metal-based catalysts such as Pt and Pd supported by  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{SiO}_2$  and zeolite exhibit high  $\text{C}_2\text{O}_5\text{OH}$  selectivity. A  $\text{Pd/CeO}_2$  catalyst shows high  $\text{C}_2\text{O}_5\text{OH}$  selectivity up to 99.2%<sup>102</sup>. However, Mo-based and Co-based catalysts represent lower  $\text{C}_2\text{O}_5\text{OH}$  selectivity up to 10%. Consequently, much research is demanded to enhance the performance of these catalysts in terms of  $\text{C}_2\text{O}_5\text{OH}$  selectivity.

For DME synthesis, a  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst shows a DME selectivity of up to 55%<sup>77</sup>. However, direct synthesis of DME through hydrogenation of  $\text{CO}_2$  poses great challenges, highlighting the need for long-term perspectives including the design of multifunctional catalyst for the interaction between methanol synthesis and methanol dehydration, enhancement of catalytic activity so as to develop an efficient product, extension of the catalyst lifetime and finally the resistance of in oxidation and sintering<sup>185</sup>.

For higher hydrocarbons synthesis, Fe-based bimetallic catalysts supported by monometallic catalysts such as Co, Ni and Pd exhibit highly HC selectivity up to 100%<sup>186</sup>. Fe-based catalysts have shown lower activity with selectivity mainly to  $\text{C}_3$  as the addition of the promoters can increase lower olefin selectivity up to 40%. Consequently, a more detailed understanding of both kinetics and mass transfer limitations in this procedure is demanded so as to optimize the catalyst performance<sup>187</sup>.

Much effort has also been dedicated to identifying the most efficient and appropriate reactor for  $\text{CO}_2$  hydrogenation process, by comparing experimental data of different reactor types including conventional units and microreactors. The most influential factor on  $\text{CO}_2$  hydrogenation to value-added chemical fuels is considered the reactor configuration, as different catalyst types and operating conditions are regarded most significant on product conversion and selectivity.

A fixed-bed reactor can be fabricated in either annular, or spherical configuration. A spherical fixed-bed reactor can be regarded as a promising alternative design compared to spherical fixed bed reactor performing under low pressure drops<sup>11, 188, 189</sup>. Another attractive alternative to enhance  $\text{CO}_2$  hydrogenation is utilising a fluidised bed reactor, as opposed to a fixed-bed reactor. Fluidised bed reactors exhibit high heat ability and specific temperature control. Furthermore, fluidised bed reactors are regarded particularly attractive due to their potential of high exothermic reactions performing<sup>6</sup>.

One of the most promising alternatives for  $\text{CO}_2$  hydrogenation to value-added chemical products is using microreactors. The necessity of microreactor technology and process performing over the last decade has proven major, especially in accelerating catalyst activity. Consequently, conventional types of reactors can be replaced by efficient and flexible micro-scale reactors.

Microwave reactors are regarded as a promising alternative for  $\text{CO}_2$  hydrogenation to value-added chemical fuels<sup>164</sup>. However, a deeper understanding of microwave-assisted catalytic reactions is required to overcome complexities, limited availabilities on dielectric properties of the catalysts and major difficulties in temperature measurements<sup>190</sup>.

## Conclusions

This review has investigated the hydrogenation of  $\text{CO}_2$  to fuels in a range of reactors. The utilisation of  $\text{CO}_2$  to several fuels and value-added chemical provides an attractive alternative to fossil fuels consumption.  $\text{CO}_2$  hydrogenation to value-added chemicals and fuels is considered a promising alternative to reduce greenhouse effect. The contribution of conventional units has gained great interest due to their potential to generate methane, methanol, ethanol, DME and hydrocarbons in industrial scale. Many of the value-added chemicals produced from this process can be utilised as gas and liquid fuels for transportation, as well as important feedstocks for several other chemical industries. Although the  $\text{CO}_2$  hydrogenation process has been investigated thoroughly in conventional reactors, such as CSTRs and FBRs, microreactors offer the opportunity to enhance the current process. Microreactors can offer higher mass and heat transfer, shorter residence times and higher  $\text{CO}_2$  conversions. Packed bed microreactors have been used for the production of hydrocarbons and methanol

from CO<sub>2</sub>. A higher intensified process can be achieved by combining the benefits of a membrane with the advantages properties of a microreactor. The membrane microreactor can perform the hydrogenation reaction under milder conditions because of higher mass and heat transfer and requires lower catalyst quantities when compared to other conventional macroscopic reactors. Microwave and microplasma reactions offer a more novel approach to the traditional reactions discussed in this study. These microreactors can operate at significantly milder reaction conditions, as well as higher conversions. Future research can be directed towards investigating the hydrogenation of CO<sub>2</sub> for the production of a variety of fuels and chemicals. In addition, other microreactor configurations could be explored to understand and enhance the heterogeneous chemical reaction. This further research could make the replacement of conventional reactors with microreactors viable in the future. Lastly, further research should investigate the scalability of these microreactors to produce fuels on an industrial scale.

## Conflicts of interest

There are no conflicts to declare.

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There are no acknowledgments to declare.

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