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Hydrogenation of carbon dioxide (CO₂) to fuels in microreactors: a review of set-ups and value-added chemicals production

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6 Hydrogenation of Carbon Dioxide (CO₂) to Fuels in Microreactors: 7 A Review of Set-ups and Value-Added Chemicals Production

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5

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10 Constantinou^{*b}

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 (CO₂) hydrogenation to value-added
13 chemicals using hydrogen (H₂) from renewable power (solar, wind) offers a unique solution. From this aspect this review
14 describes the various products, namely methane (C₁), methanol, ethanol, dimethyl ether (DME) and hydrocarbons (HC_s)
15 originating via CO₂ hydrogenation reaction. In addition, conventional reactor units for the CO₂ 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 CO₂
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 ₂ ;	Carbon dioxide
25	H ₂ ;	Hydrogen
26	CH ₄ (C ₁);	Methane
27	CH ₂ OH;	Methanol
28	C ₂ H ₂ 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 ₂ ;	Cerium oxide
49	MnO ₂ ;	Manganese oxide
50	In ₂ O ₃ ;	Indium oxide
51	NiO;	Nickel
52	TiO ₂ ;	Titanium oxide
53		
54	SiO ₂ ;	Silicon dioxide
55	Fe ₂ O ₃ ;	Iron oxide
56	K ₂ CO ₃ ;	Potassium carbonate
57	NiCo;	Catalyst
58	ZnO;	Zinc oxide
59	Co ₃ O ₄ ;	Cerium oxide
60	ZrO ₂ ;	Zirconium oxide
61	PdZn;	Catalyst
62	SBA-15;	mesoporous silica catalyst
63	ZrO ₂ ;	Zirconium Dioxide
64	γ-Al ₂ O ₃ ;	gamma-alumina
65	P;	Pressure (bar)
66	T;	Temperature (°C)
67	H ₂ 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 ³ ;	Cubic centimeter
76	min;	Minute
77	DBT;	dibenzyltoluene
78	NPs;	Nanoparticles
79	Gt;	Gigatons

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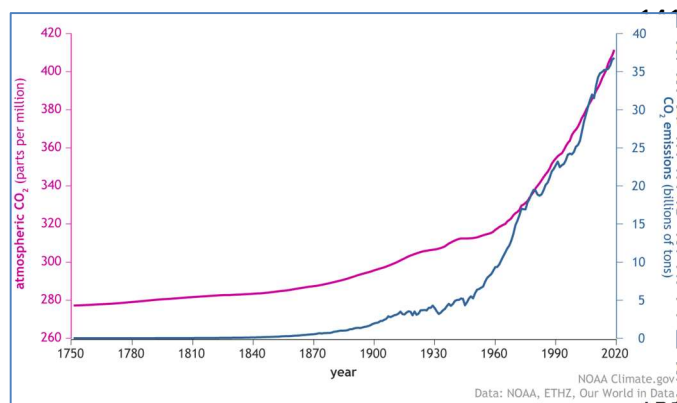
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80 Introduction

81 Excessive extraction and utilization of fossil fuels combined with
 82 continuous greenhouse gas (GHGs) emissions have led to
 83 increasing carbon dioxide (CO₂) concentration in the
 84 atmosphere¹. Recently, 33 Gt/year of CO₂ emissions were
 85 recorded, which contributes to a rapid increase in atmospheric
 86 carbon levels from 280 ppm to 410 ppm² when compared with
 87 preindustrial era. As a result of such conventional processes
 88 which utilise fossil fuels, the atmospheric CO₂ concentration is
 89 further predicted (Fig. 1) to increase to 570 ppm before the end
 90 of the century³ if no CO₂ mitigation actions are taken. Two
 91 technologies: carbon capture and storage (CCS) and carbon
 92 capture and utilization (CCU) play a significant role in reducing
 93 CO₂ emissions⁴. Generating value added products through CO₂
 94 hydrogenation utilising renewable hydrogen (H₂), produced by
 95 water electrolysis⁵, has proven to be a major challenge in order
 96 to seek alternative fuel synthesis routes⁶.



97 **Figure 1.** Schematic showing the amount of CO₂ in the atmosphere (purple line)
 98 has increased along with human emissions (blue line) since the start of the
 99 Industrial Revolution in 1750⁷.

100
 101 CCS is expected to play a vital role in limiting the GHG
 102 emissions, as well as climate change attenuation in the future.
 103 Specifically, it is considered an attractive alternative for the
 104 decarbonisation of emissions from industries and can also be
 105 merged with low carbon or carbon neutral bioenergy to
 106 produce negative emissions¹. Whereas CCU attempts both the
 107 reduction of CO₂ emissions in the atmosphere and the
 108 substitution of conventional raw materials in distinct types of
 109 industrial processes through CO₂ hydrogenation. This method
 110 focuses on using carbon free viable technologies⁸. Renewable
 111 H₂ is generated through water electrolysis by applying
 112 electricity from renewable sources such as solar and wind and
 113 is widely used for the CO₂ hydrogenation processes⁹.
 114
 115 There are several carbon utilisation methods. CO₂ can be used
 116 as a feedstock for the production of fuels and chemicals. The
 117 main products derived from CO₂ are formic acid, urea,
 118 methanol, salicylic acid and cyclic carbonates. CO₂ if often
 119 converted into fuels or chemicals through biochemical,
 120 electrochemical, photochemical, thermo-catalytic, and hybrid
 121 methods. Industrial carbon emissions can be efficiently used via
 122 mineralisation processes to produce a range of products. The

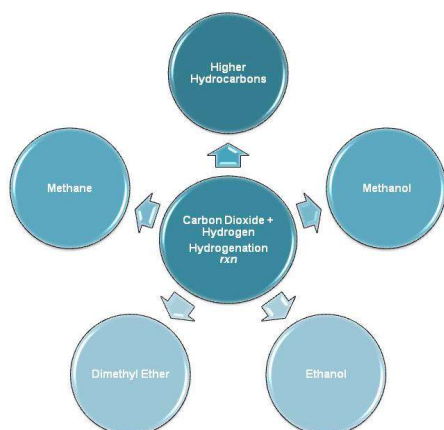
123 reaction is thermodynamically favourable, and a range of
 124 feedstocks (e.g., alkaline solid wastes and natural silicate ores)
 125 can be applied for the mineralisation processes. The
 126 mineralisation process can be divided into four main categories:
 127 direct and indirect carbonation, carbonation curing and
 128 electrochemical mineralisation¹⁰.

Potential of both conventional reactor units and microreactors
 in CO₂ 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
 added chemical fuels such as methane, methanol, ethanol, DME and
 higher hydrocarbons¹¹, due to low cost and high heat and mass
 transfer¹². Regardless of their applications, conventional units
 represent a high pressure drop, complex hydrodynamics and
 modelling^{11, 13}.

The CO₂ 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) process¹⁴. Consequently, CO₂ can be hydrogenated to
 methane (CH₄), methanol (CH₃OH), ethanol (C₂H₅OH), lower
 olefins, dimethyl ether (DME) and higher hydrocarbons^{15, 16}. A
 scheme of the main products of CO₂ hydrogenation can be seen
 in Fig. 2. The production of olefins, i.e., ethylene and propylene,
 from the hydrogenation of CO₂ 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 emissions¹⁷.
 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 fuels¹⁸.

Great efforts have recently been accomplished to prepare
 microreactors with the aim of producing chemical fuels through
 CO₂ hydrogenation¹⁹. Microreactors such as continuous flow
 microreactors^{20, 21}, micro packed-bed reactors^{22, 23}, membrane
 reactors^{24, 25}, 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 fuels²⁶.
 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.^{19, 27} Finally, the microscale volume
 capacity of microreactors have also provided efficient progress
 of continuous flow reactions since they considerably decrease

180 the quantity of materials required to improve reactor
 181 conditions²⁸. These reactors were used to synthesise chemical
 182 fuels for energy demand.



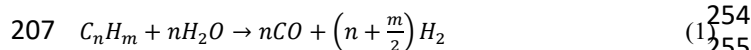
183 **Figure 2.** Schematic representation of carbon dioxide hydrogenation to value-
 184 added chemical fuels.

185 This review will provide a succinct illustration of the different
 186 routes performed to produce synthetic gases through CO₂
 187 hydrogenation according to the challenges faced by
 188 conventional units and microreactors. The contribution of
 189 conventional units during CO₂ hydrogenation process will then
 190 be described. In addition, microreactors used to produce
 191 synthetic gases will be explained. Finally, limitations between
 192 conventional units and microreactors as well as future
 193 directions will be highlighted and discussed.

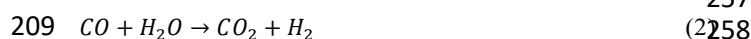
195 CO₂ Hydrogenation to Value Added Chemicals 196 Synthesis Routes

197 Hydrogen can be produced using various processes, Fig. 3 shows
 198 a brief overview of the many ways hydrogen can be obtained.
 199 Hydrogen required to react with CO₂ is conventionally produced
 200 from the steam reforming of non-renewable hydrocarbon
 201 feedstocks, and this been the preferred industrial method for
 202 several decades.

203 Typically, the steam reforming process occurs via two reactions:
 204 (1) the steam reforming of the hydrocarbons, and (2) the water
 205 gas shift (WGS) reaction²⁹.

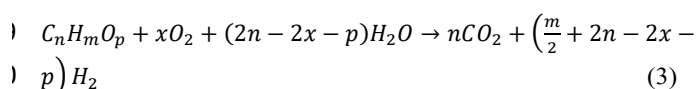


$$208 \quad \text{for } n = 1, \quad \Delta H^0_{298 K} = +206.2 \text{ kJ/mol}$$

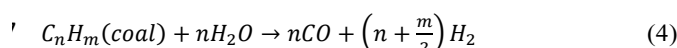


$$210 \quad \Delta H^0_{298 K} = -41.2 \text{ kJ/mol}$$

211 Another conventional method for hydrogen production is
 212 autothermal reforming. This process is like the previously
 213 described steam reforming; however, a proportion of the fuel
 214 reacts with oxygen to produce the thermal energy required in
 215 the reforming reaction which is an endothermic process. The
 216 generalised reaction for the autothermal reforming can be
 217 expressed as³⁰:

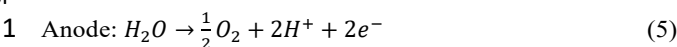


220 The value of x is related to the composition of the hydrocarbon.
 221 The gasification of coal is another significant reaction for the
 222 industrial production of hydrogen. The reaction products
 223 consist of syngas (CO and H₂), and the CO can be further
 224 upgraded to H₂ and CO₂ via the WGS reaction. The primary
 225 reaction can be given by³¹:



227 Nonetheless, the coal gasification reaction is highly
 228 endothermic and requires reaction temperatures of 1273 K to
 229 acquire the desired product yield. On the other hand, the WGS
 230 reaction is exothermic and so lower reaction temperatures for
 231 the CO conversion are needed³¹. Typically, the coal gasification
 232 reaction is performed in a reactor with a temperature of 1273
 233 K. The syngas product is then fed to another reactor which has
 234 a temperature below 673 K for the conversion of CO³².

235 The other approach is to produce the hydrogen from renewable
 236 energy sources. The electrolysis of water is one of the well-
 237 established methods to produce hydrogen as it utilises
 238 renewable and generates solely pure oxygen as a by-product.
 239 Furthermore, the electrolysis process is envisioned to use
 240 power from sustainable energy sources, such as wind, solar and
 241 biomass. However, currently, only 4% of the total hydrogen
 242 produced is coming from the electrolysis of water. This is mainly
 243 due to the economic issues³³. The various electrolytes systems
 244 for the electrolysis of water can be represented by alkaline
 245 water electrolysis (AWE), proton exchange membranes (PEM),
 246 alkaline anion exchange membranes (AEMs), and solid oxide
 247 water electrolysis (SOE). The water electrolysis process can be
 248 represented by the following³⁴:



252 The photocatalytic splitting of water with TiO₂ powders is the
 253 most basic configuration of the process, which is comprised of
 254 a sole type of semiconductor particles in continuous contact
 255 with water. Once excited by an incident photon with a greater
 256 energy than the bandgap of the semiconductor, an electron in
 257 the valence band can be pushed to the conduction band and
 258 generates a hole. Subsequently, the hole and electron separate
 259 specially and diffuse to the surface of the semiconductor to take
 260 part in the hydrogen evolution reaction and oxygen evolution
 261 reaction³⁵.

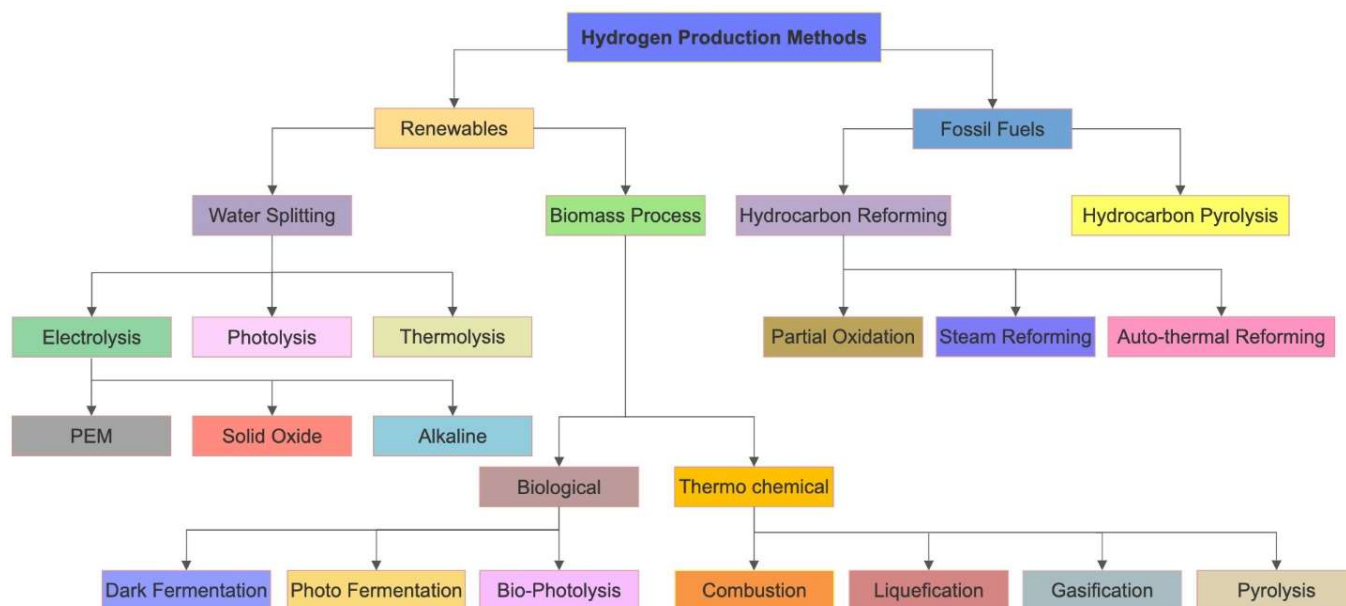


Figure 3. Overview of hydrogen production routes.

214
 215 The hydrogenation process aids the reduction of atmospheric
 216 CO₂ while producing fuels and value-added chemicals³⁶.
 217 hydrogenation to value added chemical fuels is considered
 218 beneficial process, provided that renewable H₂ is supplied³⁷.
 219 H₂ is a major utility that is typically produced from conventional
 220 petroleum reforming and could have major environmental
 221 implications. Remarkable advancements have been
 222 accomplished in the synthesis of CH₄ (C₁), methanol (CH₃OH),
 223 ethanol (C₂H₆O), dimethyl ether (DME) and higher
 224 hydrocarbons (HCs) directly from CO₂ hydrogenation. Mixture
 225 of CO₂/H₂ is required for the conversion into value added
 226 chemical fuels through the Fischer-Tropsch process and is often
 227 utilised widely in industry. Finally, synthesis of alcohols is more
 228 demanding than hydrocarbons by reason of accurate control of
 229 C-C coupling³⁹. The resulting products of CO₂ hydrogenation,
 230 such as hydrocarbons and methanol, are excellent alternative
 231 fuels for internal combustion engine with ease in storage and
 232 transportation. This alleviates many of the challenges
 233 associated with the use of fossil fuels³⁶. Table 1 provides a
 234 summary of the main catalysts which are applied for the
 235 hydrogenation of CO₂ into fuels and chemicals.

236
 237 There are some issues which exist for the conversion of CO₂ into
 238 value-added chemicals. Although the noble metal catalysts have
 239 a good performance, they are highly costly, and lack
 240 availability limits their wide scale applications for
 241 hydrogenation of CO₂ to methane and ethanol. An alternative
 242 to this would be other metal catalysts, such as Ni; however,
 243 these catalysts are highly susceptible to deactivation due to
 244 sintering and carbon poisoning⁴⁰. A similar issue exists with the
 245 Cu/ZnO/Al₂O₃ catalyst used for the hydrogenation of CO₂ to
 246 methanol. A problem faced with this catalyst is the low
 247 selectivity towards methanol caused by the reverse water gas

248 shift (RWGS) reaction. Furthermore, the catalyst activity
 249 declines rapidly due to the water product, which leads to the
 250 sintering of the Cu component during the reaction⁴¹. The typical
 251 catalysts used for ethanol synthesis can suffer from the effects
 252 of high temperature, which promote the RWGS pathway and
 253 aids the production of undesirable CO⁴². Similarly, a prominent
 254 issue with the conversion of CO₂ to higher hydrocarbons is the
 255 high selectivity towards methane and light saturated
 256 hydrocarbons⁴³.

Table 1. Summary of catalysts applied for the conversion of CO₂ into value-added chemicals.

Process Route	Catalytic System
Methane	Ru ^{50, 58, 59} , Rh ^{60, 61} , Pd ⁶² , Ni ^{53, 63} , and Co ^{40, 64}
Methanol	Cu/ZnO/Al ₂ O ₃ ^{60, 65, 66}
Ethanol	Ru ⁶⁷ , Pt ⁶⁸ , Co ⁶⁹ , Fe ⁷⁰ and Cu ^{71, 72}
DME	Cu-based ⁷³⁻⁷⁵ , solid acid catalyst ^{76, 77} and zeolites ^{78, 79}
Higher Hydrocarbons	Fe ⁸⁰⁻⁸²

CO₂ to Methane

Methane (C₁) is regarded a principal constituent of natural gases and can be successfully utilised in industry, energy and transportation sectors^{44, 45}. The production of methane through CO₂ hydrogenation is the most sustainable and convenient pathway to store significant quantities of energy generated from renewable sources⁴⁶⁻⁵⁴. CO₂ hydrogenation to C₁ reaction, initially revealed by the French chemist Paul Sabatier^{1, 55}, can be represented as^{56, 57}:



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

271 **CO₂ to Methanol** 325

272 Methanol is reported as one of the dominant chemical 326
 273 materials in the chemical and petrochemical industry through 327
 274 which methyl methacrylate, dimethyl carbonate, 328
 275 chloromethane, acetic acid, formaldehyde, methylamine, 329
 276 dimethyl terephthalate and methyl tertiary butyl ether 330
 277 generated ⁶. Methanol synthesis through CO₂ hydrogenation 331
 278 has attracted tremendous interest as noble and oxides 332
 279 supported metals have been regarded promising catalysts 333
 280 controlling both the activity and selectivity of methanol ^{60, 83, 94} 334
 281 Direct methanol (CH₃OH) generation through 335
 282 hydrogenation is represented as ^{92, 93}: 336

$$283 \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (6)$$

284 $\Delta H_{298\text{K}} = -41.1 \text{ kJ mol}^{-1}$ 337

285 338

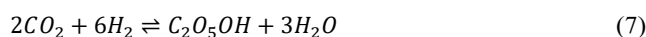
286 Remarkable progress has been made in CO₂ hydrogenation 339
 287 methanol and specifically in developing Cu and In-based 340
 288 catalysts. ⁹⁴. It is reported that over a Cu-ZnO-Al₂O₃ catalyst 341
 289 high CH₃OH selectivity up to 98.2% can be accomplished under 342
 290 conditions of P = 36 MPa and T = 220-300 °C ⁹⁵ and a In₂O₃/ZnO 343
 291 catalyst CH₃OH selectivity can be up to 99.8% under conditions 344
 292 of P = 5 MPa and T = 300 °C ⁹⁶. The remarkable selectivity and 345
 293 conversion are due to the exceedingly high-pressure conditions 346
 294 used for the study. Considering the catalytic kinetics for 347
 295 methanol synthesis, development of highly effective noble 348
 296 metal-based catalysts in terms of selectivity and stability 349
 297 demanded ⁹⁷. Hartadi et al. ⁹⁸ reported that over an Au-based 350
 298 catalyst supported by TiO₂, ZrO₂, ZnO and Al₂O₃, high CH₃OH 351
 299 selectivity up to 82% ⁹⁷ is accomplished under conditions of 352
 300 5 bar and T = 220-240 °C. Malik et al. ⁹⁹ have concluded 353
 301 over PdZn/CeO₂ and Ca-doped PdZn/CeO₂ catalysts, high CH₃OH 354
 302 selectivity of up to 100% is achieved under conditions of P = 355
 303 bar and T = 220 °C. 356

304 357

305 Lee et al. ⁴⁹ performed a techno-economic analysis for 358
 306 hydrogenation of CO₂, and methane, to methanol. Three 359
 307 processes were developed to investigate the production 360
 308 methanol from landfill gas. The first was a stand-alone process 361
 309 (L2M-SA), and the second process had a hydrogen supply (L2M- 362
 310 HS). The results from the techno-economic analysis showed 363
 311 that the L2M-HS process has poorer economics, as opposed to 364
 312 the stand-alone process, due to the excessive cost of 365
 313 hydrogen supply. Furthermore, the unit production cost (UPC) 366
 314 of the L2M-HS process was found to be around 12% higher than 367
 315 the L2M-SA process. Nonetheless, the methanol produced from 368
 316 the L2M-HS process can be economically viable with the current 369
 317 methanol market if cheaper hydrogen supply routes 370
 318 available, e.g., using hydrogen which has been produced as a 371
 319 product from industry. The study concluded that the UPC of 372
 320 methanol is approximately 392-440 \$/tonne, which is 373
 321 competitive with other conventional methanol production 374
 322 processes. Furthermore, the lower environmental emissions 375
 323 with the current process make it an environmentally friendly 376
 324 approach.

CO₂ to Ethanol

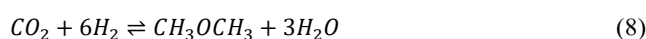
The conversion of CO₂ hydrogenation to high alcohols remains an exceptional challenge due to the understanding of parallel and successive reactions. Noble metals such as Au, Pt and Pd are reported as catalysts for direct production of ethanol from CO₂ hydrogenation with high selectivity up to 88.1% over a Pt/CO₃O₄ 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 CO₂ hydrogenation ^{39, 69, 71, 100-106}. Direct CO₂ hydrogenation to ethanol is represented below ¹⁰⁷:



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

CO₂ 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 ¹⁰⁸. The hydrogenation of CO₂ to DME has attracted great interest with several heterogeneous catalysts ^{74, 75, 77, 78, 109-112}. Direct CO₂ hydrogenation to DME is shown below:



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

Cu-ZnO-Al₂O₃ catalysts and a mesoporous HZSM-5 zeolite are used in DME synthesis, providing great resistance and improving the mass transfer process during the reactions ¹¹³. Alvarez et al. ¹¹⁴ reported that direct CO₂ hydrogenation to DME requires a bifunctional catalyst in order to perform methanol synthesis and methanol dehydration. Utilisation of γ -Al₂O₃ and H-ZMS-5 catalysts ¹¹⁵ 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. ¹¹⁴. Tokay et al. ¹¹⁶ investigated that over an Al@SBA-15 and mesoporous AlSi₃ 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/cm³.

Michailos et al. ¹¹⁷ investigated the production of DME from the captured CO₂ 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 CO₂ capture and conversion plants. A subsidised or free of charge electricity supply will make the DME price more

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

379

380 CO₂ to Higher Hydrocarbons

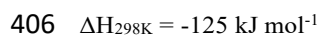
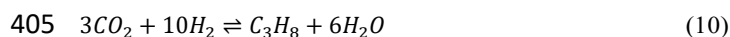
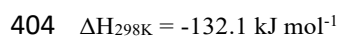
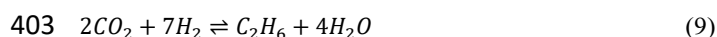
381 Higher hydrocarbons, such as light olefins and particularly
382 ethylene and propylene generation, has gained great interest in
383 the petrochemical industry¹¹⁸. Direct CO₂ hydrogenation to
384 higher hydrocarbons is described as the combination of
385 conversion CO₂ through the FT process and reverse water gas
386 shift (RWGS) reaction.

387

388 The typical catalysts applied for the process are Fe-based due to
389 their ability to catalyse both reactions. They can be utilised in
390 bulk form or as supported iron oxides. In order to diminish the
391 selectivity towards methane, the catalysts are doped with
392 oxides of Cu, K, Mn, and/or Ce¹¹⁹. The most encouraging
393 catalysts for this process are K promoted Fe/Al₂O₃ catalysts with
394 K contents of up to 0.5 mol-K mol⁻¹ of Fe. Nonetheless, these
395 catalysts experience low efficiencies for the hydrogenation of
396 CO₂. This remains a major challenge for the production of higher
397 hydrocarbons¹²⁰. Recent studies have proven that CO₂
398 hydrogenation to value added chemical fuels can be realised by
399 using the main catalysts for CO₂ hydrogenation with zeolites¹⁹.

400

401 CO₂ hydrogenation to higher hydrocarbons can be described
402 below:



407 Conventional Reactors in CO₂ Hydrogenation

408 The most used conventional reactors for the hydrogenation of
409 CO₂ are continuously stirred tank reactors (CSTRs), fluidised
410 bed reactors (FBRs) and fixed bed reactors. Fig. 4 shows a
411 schematic of these conventional reactors.

412

413 Continuously Stirred Tank Reactor (CSTR)

414 CSTRs are considered as the most conventional reactors in the
415 field of CO₂ hydrogenation. One of the operational issues with
416 CSTRs is complex non-linear behaviour. These characteristics
417 depict the requirement of a complex control system design.
418 results obtained from this non-linear analysis are significant
419 it allows the determination of difficult operating points, in order
420 to remove them. As an example, it may be useful to operate
421 around an unstable operating point, which can result in
422 observation of higher product yields¹²¹. Nonetheless, CSTRs can
423 provide wide operating range, as they can operate under steady
424 state with continuous flow of both reactants and products.
425 Fig. 5 shows a schematic of the CSTR process of the
426 hydrogenation of CO₂ to produce methane. Chiavassa et al.
427 employed a Berty-type CSTR reactor for methanol synthesis

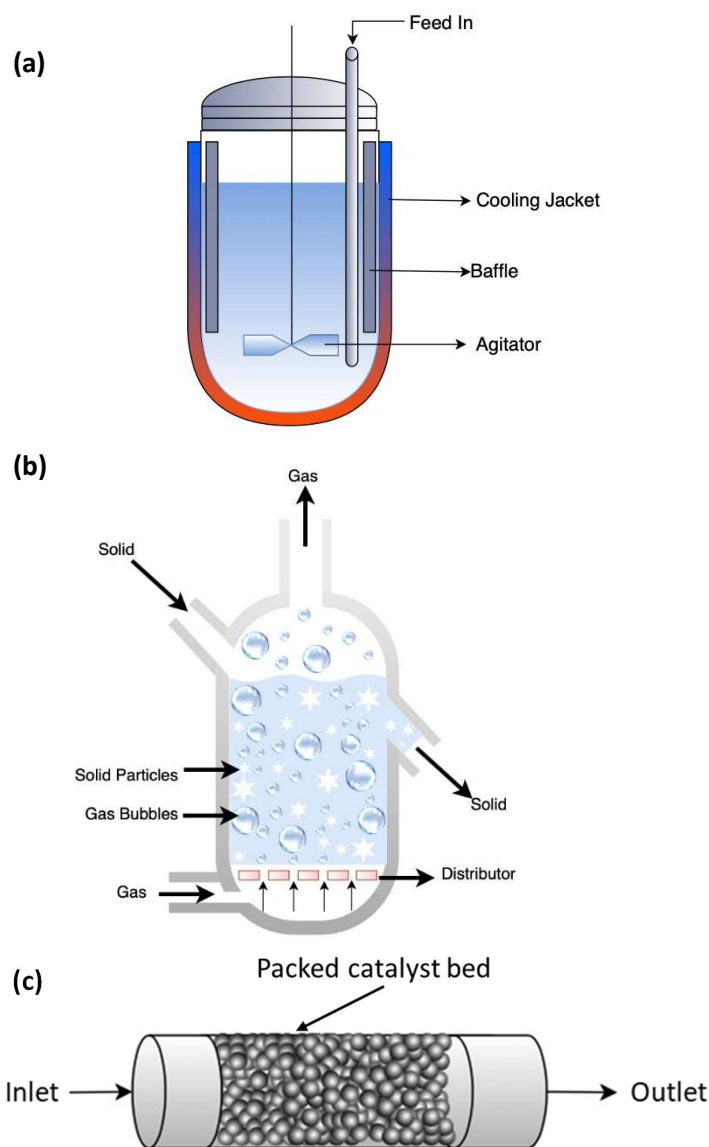


Figure 4. Schematic representation of the conventional reactors used commonly for the hydrogenation of CO₂. (a) CSTR; (b) FBR; and (c) Fixed bed reactor.

432 through CO₂/H₂ over Ga₂O₃-Pd/SiO₂ catalysts. The results
433 showed that under conditions of P = 1-4 MPa and T = 508-523
434 K, CO₂ conversion to CH₃OH was up to 70% and selectivity of
435 CH₃OH up to 50-55% was achieved.

436
437 Dörner et al.¹²⁴ used a CSTR for C₁ and C₂-C₅ higher
438 hydrocarbons synthesis, using Mn/Fe and K/Mn/Fe catalysts.
439 Hydrogenation of CO₂ was accomplished under conditions of P
440 = 13.6 atm, T = 563 K and gas hourly space velocity (GHSV) of
441 0.015 L/g s. The results showed that over Mn/Fe and K/Mn/Fe
442 catalysts, CO₂ conversion to methane was up to 34.4% and
443 41.4% and selectivity was up to 42% and 29.4%, respectively. In
444 addition, for higher hydrocarbons synthesis, the results showed
445 that over Mn/Fe and K/Mn/Fe catalysts, CO₂ conversion to C₂-
446 C₅ higher hydrocarbons was up to 41.4% and 37.7%, and the
447 selectivity reached 62.4% and 55.3%, respectively.

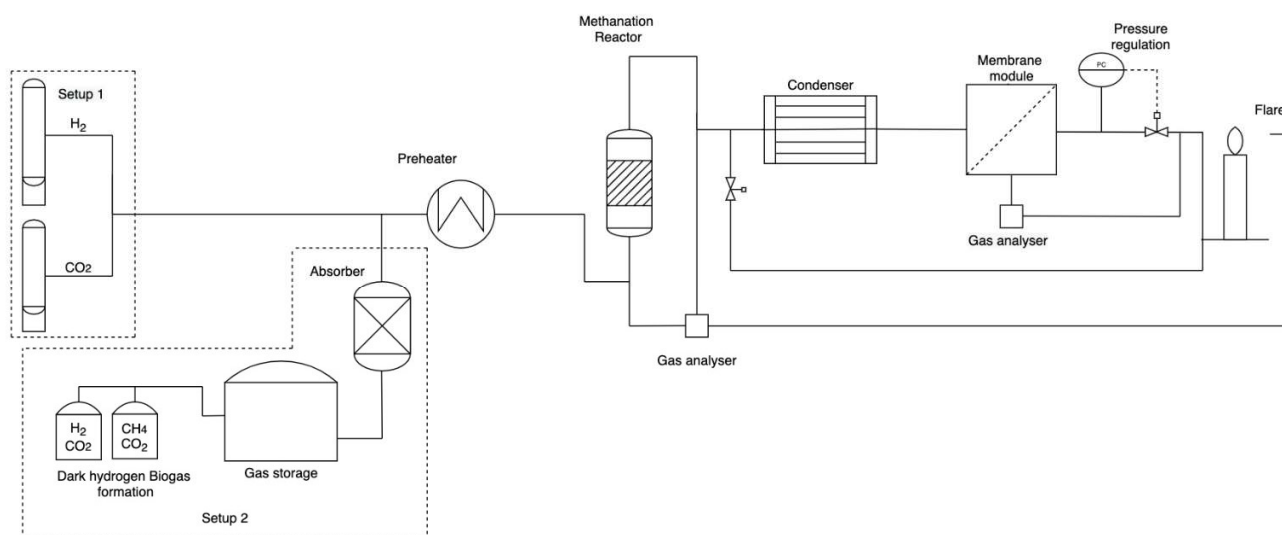


Figure 5. Flow sheet of the connected processes for CO₂ hydrogenation to methane using a CSTR.

428
 429 Lefebvre et al.¹²⁵ used a CSTR reactor to identify the study
 430 the three-phase CO₂ methanation reaction, applying
 431 commercial Ni/SiO₂ catalyst, suspended in the liquid phase
 432 Feed gases were heated in a preferred temperature between
 433 220 °C and 320 °C and mixed in a tempered feed tank.
 434 results showed that under conditions of P = 1 atm and T =
 435 320 °C, CO₂ conversion to methane could not increase
 436 further for an agitator speed above ca. 1000 L/min and
 437 selectivity during the process was up to 95%.
 438
 439 Kirchbacher et al.¹²⁶ also used a CSTR reactor to produce
 440 derived from the reaction of CO₂ and renewable H₂, generated
 441 by water electrolysis. For methane synthesis through
 442 hydrogenation, two main processes were achieved. Initially,
 443 high H₂/CO₂ ratio was applied to prevent thermal effects of
 444 spherical catalyst Meth 134[®], which provides a high
 445 conversion to CH₄ that is approximately 80%. Methanation
 446 process was conducted at three pressure levels of 6, 10, 14
 447 and a GHSV of 3.000, 4.000, 5.000 and 6.000 h⁻¹ under
 448 conditions of T = 395–425 °C. Secondly, under semi-
 449 conditions biogas and synthetic H₂ were employed to generate
 450 methane. The feed gas composition was investigated by
 451 pressure levels of 6, 8, 10, 12 and 14 bar. However, GHSV was
 452 limited to 4.000 h⁻¹. Methane productivity reached a level
 453 85% v/v under condition of P = 14 bar.
 454
 455 García-Trenco et al.¹²⁷ used a CSTR reactor to generate
 456 methanol through CO₂ hydrogenation, applying bimetallic Pd
 457 nanoparticles as catalysts. The results showed that Pd
 458 catalysts reduced methanol activity up to 50%, whereas
 459 catalyst including Pd/In intermetallic nanoparticles (Ni)
 460 exhibited high CH₃OH rate up to 70% and high CH₃OH selectivity
 461 up to 90%. Furthermore, the optimum Pd/In-based catalyst
 462 displayed an improvement in stability- the methanol production
 463 rate decreased by 20% after 120 h run, compared with 30% for
 464 the Cu/ZnO/Al₂O₃ catalyst (after 25 h).

465
 466 A further study performed by García-Trenco et al.¹²⁸
 467 investigated the hydrogenation of CO₂ to methanol using
 468 colloidal Pd₂Ga-based catalysts in a CSTR reactor. The colloidal
 469 Pd₂Ga-based catalysts shown 2-fold higher intrinsic activity than
 470 commercial Cu-ZnO-Al₂O₃ (60.3 and 37.2 × 10⁻⁹ mol_{MeOH} m⁻² s⁻¹)
 471 and 4-fold higher on a Cu or Pd molar basis (3330 and 910
 472 μmol mmol_{Pd or Cu}⁻¹ h⁻¹) in liquid phase at a reaction pressure of
 473 50 bar. The results showed a good correlation between the
 474 intrinsic activity and the content of Ga₂O₃ surrounding the
 475 Pd₂Ga nanoparticles (XPS), indicating that methanol is produced
 476 via a bifunctional mechanism concerning both phases. A steady
 477 decrease in methanol selectivity (60 to 40%) was observed
 478 when temperature was raised (190–240 °C) whilst an optimum
 479 methanol production rate was observed at 210 °C. Nonetheless,
 480 when compared to the conventional Cu-ZnO-Al₂O₃, which
 481 suffered from around a 50% loss of activity over 25 h time on
 482 stream, the Pd₂Ga-based catalysts sustained activity over this
 483 time frame.

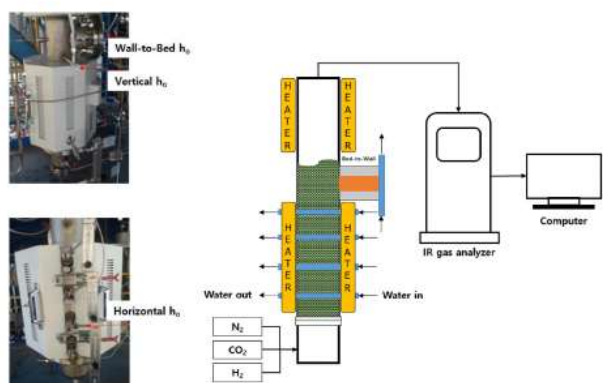
484
 485 In industry, it is common to utilise multifunctional metallic
 486 copper and zinc oxide catalyst on alumina (CZA). Huš et al.¹²⁹
 487 investigated experimentally, and via multiscale modelling, of
 488 commercial-like catalyst (Zn₃O₃/Cu) and three other Cu/metal
 489 oxide combinations (Cr₃O₃/Cu, Fe₃O₃/Cu, and Mg₃O₃/Cu),
 490 synthesised by co-precipitation. The results showed that the
 491 formate species pathway (HCOO → H₂COO → H₂COOH → H₂CO
 492 → H₃CO) dominates on the studied Cu-based catalysts.
 493 Although, Zn₃O₃/Cu exhibited the highest conversion and a
 494 moderate CH₃OH product selectivity, the former was smaller for
 495 Mg₃O₃/Cu. Furthermore, Cr₃O₃/Cu was ideal in terms of yield,
 496 but with exceptionally low CH₃OH productivity, whereas
 497 Fe₃O₃/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 CO₂ hydrogenation to value chemical fuels, conversion
 504 syngas, selectivity and economic feasibility⁴. Kim et al.¹³⁰ 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, CO₂ conversion to olefins was up to
 511 46.8%, and olefins selectivity up to 89.3% was accomplished.

513 Nam et al.¹³¹ used a bench-scale bubbling fluidised bed reactor
 514 (shown in Fig. 6) for CO₂ 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 CO₂ hydrogenation to methane.
 518 bubbling fluidised reactor (diameter of 0.14 m and height of 1.0
 519 m) was encircled by an electrical heater. The results showed
 520 that a high CO₂ conversion to CH₄ up to 98% and CH₄ 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/m².

524 Jia et al.¹³² employed a fluidised bed reactor for direct
 525 hydrogenation to methane, applied a Ni-Co based catalyst
 526 supported on TiO₂-coated SiO₂ spheres. A bench-scale fluidised
 527 bed reactor was utilised for CO₂ 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, CO₂ conversion to
 532 methane was up to 52%, and CH₄ selectivity up to 97% was
 533 achieved.



534 Figure 6. Bench scale fluidised bed reactor (left) and schematic diagram (right)¹³¹
 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 bed¹³³. In fixed bed reactors, gas, and liquid flow
 541 below the catalyst bed from the top of the reactor to the

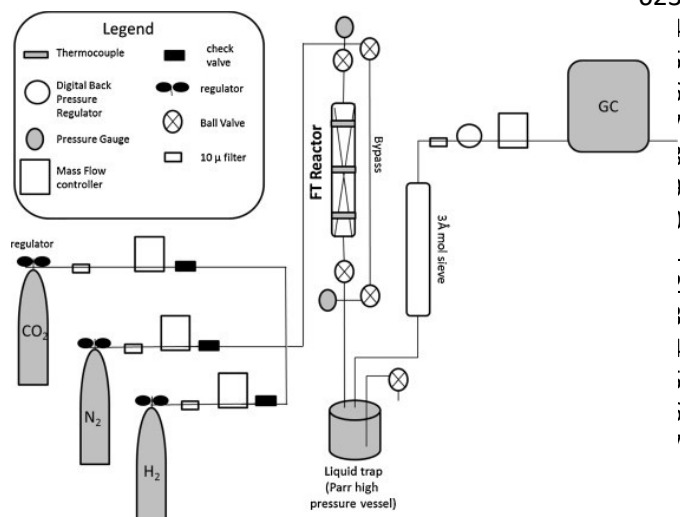
542 bottom, without stirring. Furthermore, CO₂ and H₂ are in direct
 543 contact with the catalyst particles¹³⁴. One of the major points
 544 in fixed bed reactors is the temperature control in exothermic
 545 reactions. The desired minimal CO₂ conversion can reach 90%.
 546 Finally, the reaction time varies with the catalyst due to the
 547 generation of H₂O and the reaction rates¹³⁵.

548 Ducamp et al.¹³⁶ used a cylindrical annular fixed bed reactor
 549 (inner diameter of 20 mm, outer diameter of 50 mm and length
 550 of 34 mm) to produce methane, by applying a commercial
 551 catalyst made of a Ni active phase scattered on alumina trilobe
 552 extrudates, and to analyse CO₂ and C₂H₆. The results showed
 553 that under reaction conditions of pressure from 0.4 to 0.8 MPa
 554 and a temperature between 200 °C and 275 °C, CO₂ conversion
 555 to CH₄ was up to 85% and 89%, respectively.

556 Jaffar et al.¹³⁷ used a fixed bed reactor containing a gas
 557 preheater to generate methane using a 10% wt. Ni-Al₂O₃
 558 catalyst. The results showed that under condition of
 559 temperature 360 °C methane yield up to 57.6% and methane
 560 selectivity up to 98% was achieved. Kiewidt et al.¹³⁸ used a fixed
 561 bed reactor to produce methane. A 5% wt Ru-based catalyst
 562 supported by ZrO₂ loaded directly in the reactor with diluted
 563 catalyst powder. The results showed that under reaction
 564 conditions of pressure 10 bar and temperature 300 °C, methane
 565 yield up to 90% was generated.

566 Castellani et al.¹³⁹ used a stainless mono tubular fixed bed
 567 reactor CO₂ methanation. The results showed that under
 568 reaction conditions of pressure from 2 to 20 bar and
 569 temperature between 250 °C and 400 °C, methane conversion
 570 of 31.36%, methane content up to 97.24% and CO₂ conversion
 571 up to 99.6% was achieved. Willauer et al.¹³⁴ employed a fixed
 572 bed reactor (shown in Fig. 7) (stainless steel tube) for direct
 573 synthesis of hydrocarbons through CO₂ hydrogenation, using a
 574 γ -Al₂O₃ supported modified iron-based catalysts. The results
 575 showed that under conditions of P = 265 psig and T = 300 °C,
 576 CO₂ conversion of C₂-C₅ hydrocarbons was up to 41.4% and
 577 selectivity was up to 62.4%.

583



584

585 Figure 7. Flow sheet for CO₂ hydrogenation using a fixed bed reactor¹³⁴ (copyright
586 permission obtained from Elsevier).

587

588 Pastor-Pérez et al.¹⁴⁰ used a fixed bed reactor for direct
589 hydrogenation to methane and applied Ni/CeO₂-ZrO₂ catalysts
590 promoted with Mn and Co. CO₂ methanation process was
591 conducted in a vertical continuous fixed bed quartz reactor
592 (inner diameter of 10mm), using 250 mg of the catalyst. The
593 results showed that under conditions of T = 400 °C, CO
594 conversion to CH₄ up to 70% and CH₄ selectivity up to 99% was
595 achieved. Furthermore, Bradley et al.¹⁴¹ employed a fixed bed
596 reactor to identify the role of the catalyst environment on
597 hydrogenation by applying a Macrolite® supported iron-based
598 catalysts. The results showed that under conditions of T = 280-
599 320 °C, CO₂ conversion to methane and C₂-C₅ higher
600 hydrocarbons up to 22-36%, CH₄ selectivity up to 26% and C₂-C₅
601 higher hydrocarbons selectivity up to 60-69% were achieved.

602

603 Zhang et al.¹⁴² investigated the selective hydrogenation of
604 CO₂ and CO into olefins over sodium- and zinc-promoted iron
605 carbide catalysts in a fixed bed reactor. The results showed that
606 the selectivity of C₂-C₁₂ olefins reached 78%, and the space-
607 time yield of olefins attained as high as 3.4 g g_{cat}⁻¹h⁻¹ in
608 CO₂ hydrogenation. Furthermore, the intrinsic formation rate
609 of C₂-C₁₂ olefins in CO hydrogenation was approximately twice
610 higher when compared to that in CO₂ hydrogenation. The
611 hydrogenation of CO₂ to olefins proceeds via CO intermediate
612 over the developed catalyst.

613

614 Park et al.¹⁴³ studied the CO₂ hydrogenation to formic acid over
615 heterogenised ruthenium catalysts using a fixed bed reactor
616 with separation units. The results showed that the Ru/bpyTN-
617 30-CTF catalyst prepared using the bpyTN-30-CTF support
618 exhibits adequate catalytic activity for commercialisation.
619 Under the continuous process, the catalyst displays
620 considerable catalytic performance with the highest
621 productivity of 669.0 g_{form.} g_{cat}⁻¹ d⁻¹ with CO₂ conversion of
622 44.8% for a superficial gas velocity of 72 cm s⁻¹. In addition,
623

623

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.¹⁴⁴ studied the hydrogenation of CO₂ using magnetic
nanoparticles in a fixed bed reactor. The results showed that
high activity and selectivity were obtained at 493 K, when
MnFe₂O₄ 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-MnFe₂O₄, 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 CO₂ to MeOH
to alleviate the effects of greenhouse gases.

638 Microreactors for CO₂ Hydrogenation

639 Microreactors have been widely used to generate synthetic
640 gases and liquid fuels from direct CO₂ hydrogenation, supported
641 by reverse water gas shift reaction and Fischer-Tropsch (FT)
642 process, in order to produce methane, methanol, ethanol, DME
643 and hydrocarbons. The desirable characteristics of
644 microreactors in the field of energy technology has attracted
645 great attention in recent years. The benefits of microreactors,
646 such as enhanced mass and heat transfer, shorter residence
647 time and lower pressure drops, make microreactors an
648 interesting option for gas conversion processes in which
649 conversion and selectivity are closely linked to the mass and
650 heat transfer properties of the reactor and catalyst¹⁴⁵. In this
651 section, the hydrogenation of CO₂ in packed bed and membrane
652 microreactors, as well as microwave and microplasma reactors.
653 Fig. 8 shows a schematic representation of the membrane and
654 microplasma reactors.

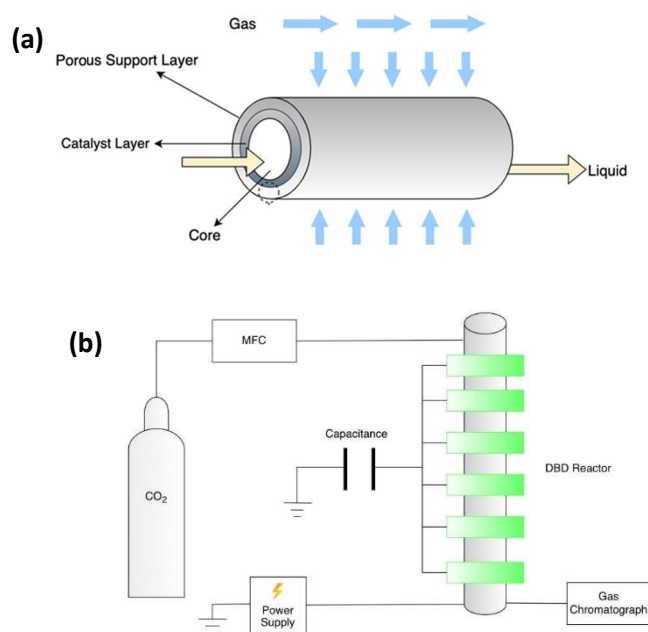
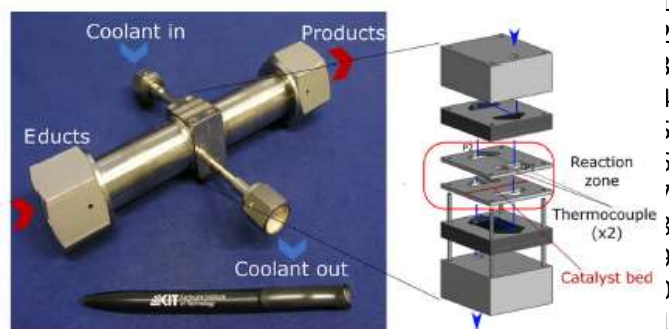


Figure 8. Schematic representation of (a) membrane microreactor; and (b) microwave reactor set-up.

657 **Packed Bed Microreactors**

658 In packed bed microreactors, the heterogeneous catalyst
 659 packed in a specific form into a microchannel. A packed bed
 660 microreactor provides easy loading and replacement of
 661 catalyst¹⁴⁶. Farsi et al.¹⁴⁷ employed a microstructured packed
 662 bed reactor (shown in Fig. 9) with internal cross-flow cooling
 663 channel to investigate the kinetics of CO₂ hydrogenation
 664 methane by applying a 17% wt Ni₃Fe/ γ -Al₂O₃. The shorter bed
 665 length offered shorter contact time and prevented higher
 666 pressure drops. The results showed that the catalyst operated
 667 for over 120 min and under reaction conditions of 2 to 18 bar
 668 and 300 °C–450 °C, CO₂ conversion to CH₄ up to 92% and
 669 methane selectivity up to 99% was achieved. Kreitz et al.¹⁴⁸
 670 used a microstructured fixed bed reactor to produce methane
 671 consisting of a 2 mm square channel. Spherical catalyst particles
 672 of 0.4 mm diameter were used to control the pressure drop and
 673 catalyst inventory. The results showed that under reaction
 674 conditions of pressure 8 bar and temperature 280 °C, a high CO₂
 675 conversion of 97.8 % was accomplished.



676 **Figure 9.** Micro-structured packed-bed reactor¹⁴⁷ (copyright permission obtained
 677 from Elsevier).

678 Belimov et al.¹⁴⁹ used a microstructured packed bed reactor
 679 methanation process of CO/CO₂ mixtures by applying
 680 commercial Ni-based catalyst to enhance the process. The
 681 results showed that after 2h of the reaction and under
 682 conditions of 200 °C to 900 °C, CO₂ conversion up to 95%
 683 CH₄ selectivity up to 97% was achieved.

684 The hydrogenation of CO₂ to methanol has often been one
 685 the most effective and economical methods of reducing the
 686 CO₂ emissions. Jiang et al.¹⁵⁰ studied the catalytic hydrogenation
 687 CO₂ to methanol over Pd/In₂O₃/SBA-15 catalysts in a packed
 688 bed microreactor. It was found that the Pd/In₂O₃/SBA-15
 689 catalysts exhibited superior catalytic activity with 83%
 690 methanol selectivity and 12.6% CO₂ conversion, corresponding
 691 to a STY of $1.1 \times 10^{-2} \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ under reaction conditions
 692 260 °C, 5 MPa and $15,000 \text{ cm}^3 \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. Moreover, the authors
 693 found no apparent deactivation of the catalyst during the 120
 694 h on stream, which implies a promising industrial application
 695 for the CO₂ hydrogenation for methanol synthesis.

696 Fang et al.¹⁵¹ developed a hybrid catalyst/adsorbent consisting
 697 of Cu-ZnO-ZrO₂ supported on hydrotalcite (named CZZ@HT)

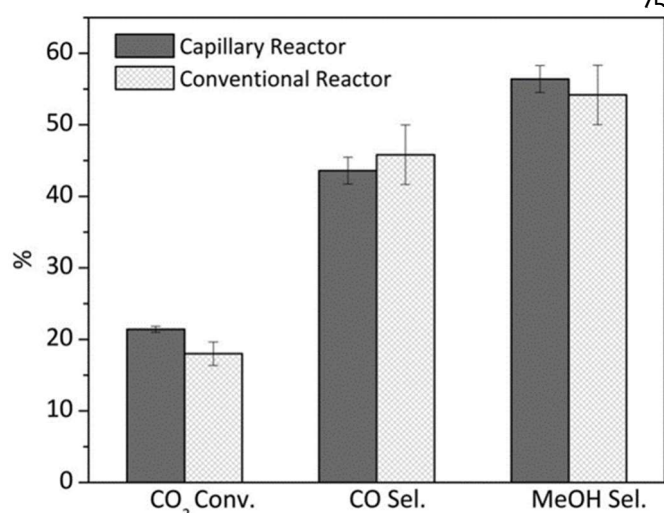
and performed the hydrogenation studies in a packed bed
 microreactor. The experimental results obtained using the
 packed bed microreactor demonstrated a methanol selectivity
 of 83.4% and a S_{MeOH}/S_{CO} ratio of 5 in products. A control
 experiment was performed by substituting the hydrotalcite 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-ZrO₂ 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.¹⁵² investigated the structure-activity relationships of
 transition metal (Cr, Mn, Fe, Co, Ni) promoted copper-catalyst
 in direct CO₂ 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 H₂:CO₂ mole ratio of 3:1, the
 catalyst presented the highest methanol yield of 10.4%. The
 CO₂ conversion achieved was 10.5% and the methanol
 selectivity was 98.6%.

Koh et al.¹⁵³ synthesised a series copper-catalysts, Cu-ZnO-MnO
 (CZM), supported on morphologically distinct siliceous porous
 carriers (SBA-15, MCF, KIT-6) for the direct CO₂ 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 CO₂ conversion (8.2%) and highest methanol
 production rate ($105.3 \text{ mol} / \text{kg}_{\text{cat}} \cdot \text{h}$) at low reaction temperature
 (180 °C). The methanol selectivity attained was $\geq 99\%$ in all the
 experiments.

Liang et al.¹⁴⁵ investigated the hydrogenation of CO₂ 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% CO₂ 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.

700 The hydrogenation of CO₂ into methanol is an exothermic
 701 reaction and according to thermodynamics high pressure
 702 lower temperature is beneficial to achieve high conversion
 703 CO₂ into methanol. Typical CO₂ hydrogenation pressures are
 704 to 10 MPa. Bansode et al.⁹⁵ exploited the advantages of high
 705 pressure for this reaction by performing the reactions up to
 706 MPa in a microreactor to obtain almost complete conversion of
 707 CO₂ into methanol. Moreover, they also investigated the
 708 oxidation state of Cu in active catalyst under pressure of 20 MPa
 709 in a specially designed capillary microreactor. It was found that
 710 the Cu always remained in metallic state under the employed
 711 conditions of pressure and temperature¹⁵⁴. In addition, the
 712 performance of such capillary microreactor was also elucidated
 713 and compared with conventional reactor system. As it can be
 714 seen in Fig. 10, almost identical catalytic activity was achieved
 715 in both reactors, detailing the advantage of capillary
 716 microreactor to use *in situ/operando* techniques which
 717 normally not possible with conventional systems.



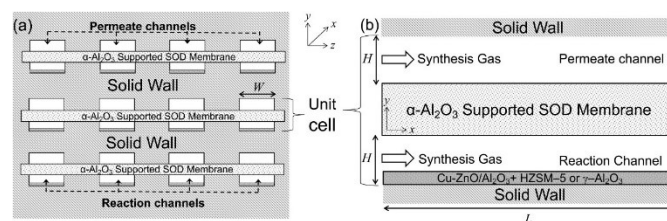
718 **Figure 10.** Catalytic performance in terms of CO₂ conversion and selectivity to CO
 719 and methanol (MeOH) in CO₂ hydrogenation using the capillary reactor and
 720 conventional microreactor¹⁵⁴ (copyright permission obtained from AIP).

721 Tidona et al.¹⁵⁵ employed even higher pressures of 95 MPa in
 722 stainless steel microreactor. The study shown that
 723 compression of CO₂ and H₂ accounts only for 26% of the total
 724 energy consumption whereas the main cost was associated
 725 with the hydrogen. This increase in pressure enhanced
 726 space time yield by 15 times compared to literature reports.
 727 Although packed bed microreactors have proved valuable for
 728 the hydrogenation of CO₂, these reactors can suffer from high
 729 pressure drops when using small catalyst pellets. Furthermore,
 730 the use of solid catalyst particles can lead to plugging or fouling
 731 of the microchannels, leading to the obstruction of the
 732 continuous flow. To mitigate these effects, catalytically active
 733 metals can be used to cover the inside walls of the microreactor
 734 or can be placed on poles in the reactor channels, as seen in
 735
 736

flow microreactors and coated wall microreactors¹⁸.
 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^{156,157}.

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 reactors¹⁵⁸. Koybasi et
 al.¹⁵⁹ investigated the hydrogenation of CO₂ to DME in a
 membrane microreactor (Fig. 11). The reactor is comprised of
 identical permeate and catalyst coated reaction channels,
 separated by an α -Al₂O₃ supported water-selective sodalite
 (SOD) membrane layer. The results showed that implementing
 the SOD membrane layer enhanced the CO₂ 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 CO₂/CO_x ratio of 0.5
 and a H₂/CO_x 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 CO₂/CO_x 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 CO₂ conversion and DME yield.



768 **Figure 11.** Schematic representation of membrane microreactor used for the
 769 hydrogenation of CO₂¹⁵⁹ (copyright permission obtained from Elsevier).

770 Wang et al.¹⁶⁰ studied the hydrogenation of CO₂ to methanol
 771 using ZnO/t-ZrO₂ (ZrO₂ tetragonal phase) composite oxides in a
 772 membrane separation microreactor. The reaction conditions
 773 were a temperature of 320 °C, pressure 3 MPa, GHSV = 12,000
 774 ml g⁻¹ h⁻¹ and a H₂/CO₂ ratio of 3:1. It was found that different
 775 catalyst preparation techniques substantially altered the phase
 776 structure properties of the Zn/Zr hybrid interfaces and the CO₂
 777 hydrogenation to methanol reaction. The microreaction
 778 synthesis technique had superior technical advantages due to
 779 the unique properties of the microchannels, such as an
 780 enhanced mixing efficiency and improved mass and heat
 781 transfer. The results showed that the solid solution produced
 782 from the microreaction demonstrated a superior catalyst
 783
 784

785 performance, temperature stability and catalyst regeneration
 786 perform. This was because of a highly constant solid solution
 787 structure, and rich oxygen vacancy defects. It was found that
 788 the CO₂ conversion, CH₃OH selectivity, and methanol space
 789 time yield were 9.2 %, 93.1 %, and 0.35 g_{MeOH} h⁻¹g_{cat}⁻¹,
 790 respectively.
 791
 792 Despite the advantages membrane microreactors have offered
 793 for the hydrogenation of CO₂, there are limitations which exist
 794 for this technology. For example, any alterations in the surface
 795 chemical and physical properties can influence the performance
 796 of the system which directly affects the surface tension,
 797 adsorption and electro-osmosis features substantially.
 798 Moreover, small particles in the fluid zone can cause blocking
 799 the microchannels in the reactor¹⁶¹. Microplasma reactors
 800 have become increasingly attractive due to their reduced power
 801 requirements, portability, and diminished power requirements.
 802 Furthermore, microplasmas provide a solution to the catalytic
 803 issues observed with the previously mentioned microreactors
 804¹⁶².
 805
 806 **Microwave and Microplasma Reactors**
 807 The application of microwave technology in chemical processes
 808 is regarded well established in organic synthesis and materials
 809 processing. Microwave reactors can be efficient in CO₂
 810 hydrogenation to value-added chemical fuels, using
 811 heterogeneous catalysts. Reactor design plays a major role both
 812 in modelling and fabrication in microwave technology¹⁶³.
 813
 814 de la Fuente et al.¹⁶⁴ employed a non-equilibrium microwave
 815 plasma reactor for the reduction of CO₂ with H₂. CO₂
 816 hydrogenation was investigated in a non-thermal microwave
 817 discharge. A solid-state microwave generator with power of
 818 W was applied to enhance the microwave energy to the plasma
 819 reactor. Plasma performed under pressure 7 to 200 mbar, while
 820 most of the reactants operated at pressure between 20 and
 821 mbar. The results showed high CO₂ conversion to value-added
 822 chemical fuels up to 82%. Innovative microwave technology
 823 could be performed in order to define both conversion and
 824 selectivity for reactants and products under efficient control of
 825 temperature and pressure conditions¹⁶⁵.
 826
 827 Chen et al.¹⁶⁶ studied the CO₂ hydrogenation in a microwave
 828 plasma reactor. The pulsed microwave plasma generation
 829 discharge took place in a quartz tube. An oil coolant is passed
 830 between the inner and outer tube. The results showed that the
 831 CO₂ conversion is significantly enhanced when the Ar plasma
 832 activated NiO/TiO₂ catalyst has an NiO content is approximately
 833 10 wt.%. Furthermore, the total CO₂ conversion fell from
 834 to 14% for the pure CO₂ dissociation for a H₂:CO₂ mixture ratio
 835 of 1:9. This was due to the presence of hydrogen lowering the
 836 temperature of the electrons and diminishing the vibrational
 837 effects of CO₂. The hydrogenation of CO₂, which occurred in a
 838 non-equilibrium microwave plasma reactor, reached a total
 839 conversion of 85% with an energy efficiency of approximately
 840 6% and a CO₂ selectivity of 100%.

Wang et al.¹⁶⁷ performed the decomposition of pure CO₂ into
 CO and O₂ in a segmented electrode dielectric barrier discharge
 (DBD) microplasma reactor at ambient pressure. The results
 showed that a relatively higher CO₂ conversion and energy
 efficiency could be obtained at the propitious condition of
 longer interval between adjacent electrodes and smaller barrier
 thickness, and the highest CO₂ 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 CO₂ molecules occurred. These
 factors are the main reasons for the enhanced CO₂
 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 volume¹⁶².

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 CO₂ 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 described¹⁶⁸.
 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 time¹⁶⁹. 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
 elutriation¹⁷⁰⁻¹⁷².

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

	Microreactors	Conventional Reactors
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.

841 Fixed bed reactors are subject to high pressure drops
842 Moreover, these reactors tend to be more complex, while they
843 exhibit higher costs¹⁷³. Multiple fixed-bed reactors in parallel
844 are demanded for larger plants. Preventing high pressure in
845 reactor tube, large-scale catalyst particles are required
846 resulting in lower effectiveness factors (lower catalyst activity
847 per unit mass, resulting from difficulties of reactants to scale
848 in the core of the catalyst particle). Another major limitation
849 fixed-bed reactors face is lower heat transfer from the catalyst
850 bed and the variation of temperature into the tubes. This fact
851 results in a) difficulty in controlling the product composition
852 hot spots in the catalyst bed that may be led to both catalyst
853 sintering and reactor instability, and c) lower conversions of
854 40% to prevent high temperatures (in that case unreacted feed
855 can be recycled)¹⁷⁴.
856
857 Microreaction technology is considered a field that has gained
858 significant attention due to its great performance in operating
859 processes compared to conventional units. Microreactors offer
860 efficient manipulation of reactions, great response time,
861 accurate control of environmental conditions, reduced
862 consumption of both reagents and catalysts and also provide
863 the opportunity of an integrated instrumentation, an in-line
864 optimisation and automation methods¹⁷⁵. However,
865 microreactors exhibit major limitations, occurred
866 imperfections of microreaction technology during chemical
867 processes. Highly fabrication cost, incompatibility over some
868 and high economics of scaling up has led to inadequate
869 industrial acceptance. Moreover, microreactors perform with
870 shorter residence times, requiring the achievement of
871 reactions. Fast reactions demand highly active catalysts, which
872 should be stable in the microreactor. Consequently,
873 microreactors cannot be applied as a replacement for classical
874 processes yet¹⁷⁶.
875

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 milliseconds²⁷. Moreover, automated micro platforms have been reported in enabling design of experiments for optimization of operations conditions and reaction kinetics definition¹⁷⁷. 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 resolved¹⁷⁵.

Future Perspectives in CO₂ Hydrogenation

The hydrogenation of CO₂ is considered a sustainable procedure and a promising alternative for CO₂ utilisation. However, CO₂ is regarded chemically stable and thermodynamically unfavourable. High reaction heat, different types of reactors design and sensitive catalysts, indicates CO₂ hydrogenation to value-added chemical fuels (methane, methanol, ethanol, DME and higher hydrocarbons) a challenging procedure for further research and development.

876 For methane generation, catalysts containing noble metals supported
 877 as Ru, Rh, Ir and Pt supported by TiO₂, SiO₂, Al₂O₃ exhibit high
 878 CH₄ selectivity up to 100%, as regarded the most active metal
 879 Ni-based catalysts such as Ni/Ce_{0.72}Zr_{0.28}O₂¹⁷⁸ and Ni/MCM-41
 880¹⁷⁹ represent high CH₄ selectivity up to 99% and 90%
 881 respectively. One of the crucial problems in Ni-based catalysts
 882 is considered the deactivation of the catalyst at high
 883 temperatures due the interaction of metal particles with CO
 884 formation of nickel subcarbonyls⁴. Consequently, this problem
 885 highlights the need for process optimisation in this field.
 886
 887 For methanol production, catalysts consisting of Cu represent a
 888 major role in improving methanol synthesis through the
 889 hydrogenation of CO₂, with the most active catalyst component
 890 supported by ZnO, ZrO₂, CeO₂, Al₂O₃ and SiO₂^{180, 181}
 891 Cu/ZnO/Al₂O₃ catalyst exhibits high CH₃OH selectivity up to
 892¹⁸². However, the bifunctional catalyst system poses major
 893 challenges for the application of a Cu/ZnO-based catalyst.
 894 considered a thermally unstable component and the size of
 895 crystallites can be increased at high temperatures, resulting
 896 the loss of the active surface and Cu sintering⁷³. Furthermore,
 897 Cu-based catalysts can be poisoned, and a lower lifetime
 898 be occurred¹⁸³. Consequently, this challenge should emphasize
 899 the need for further research, as well as catalyst regeneration.
 900
 901 For ethanol synthesis, noble metal-based catalysts such as Pt
 902 and Pd supported by TiO₂, CeO₂, SiO₂ and zeolite exhibit high
 903 C₂H₅OH selectivity. A Pd/CeO₂ catalyst shows high C₂H₅OH
 904 selectivity up to 99.2%¹⁰². However, Mo-based and Co-based
 905 catalysts represent lower C₂H₅OH selectivity up to 10%
 906 Consequently, much research is demanded to enhance the
 907 performance of these catalysts in terms of C₂H₅OH selectivity.
 908
 909 For DME synthesis, a Cu/ZnO/Al₂O₃ catalyst shows a DME
 910 selectivity of up to 55%⁷⁷. However, direct synthesis of DME
 911 through hydrogenation of CO₂ poses great challenges,
 912 highlighting the need for long-term perspectives including the
 913 design of multifunctional catalyst for the interaction between
 914 methanol synthesis and methanol dehydration, enhancement
 915 of catalytic activity so as to develop an efficient product,
 916 extension of the catalyst lifetime and finally the resistance of
 917 in oxidation and sintering¹⁸⁵.
 918
 919 For higher hydrocarbons synthesis, Fe-based bimetallic
 920 catalysts supported by monometallic catalysts such as Co, Ni,
 921 and Pd exhibit highly HC selectivity up to 100%¹⁸⁶. Fe-based
 922 catalysts has shown lower activity with selectivity mainly to C₁-
 923 as the addition of the promoters can increase lower olefin
 924 selectivity up to 40%. Consequently, a more detailed
 925 understanding of both kinetics and mass transfer limitations
 926 this procedure is demanded so as to optimize the catalyst
 927 performance¹⁸⁷.

Much effort has also been dedicated to identifying the most efficient and appropriate reactor for CO₂ hydrogenation process, by comparing experimental data of different reactor types including conventional units and microreactors. The most influential factor on CO₂ 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^{11, 188, 189}. Another attractive alternative to enhance CO₂ 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 performing⁶.

One of the most promising alternatives for CO₂ 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 CO₂ hydrogenation to value-added chemical fuels¹⁶⁴. 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 measurements¹⁹⁰.

Conclusions

This review has investigated the hydrogenation of CO₂ to fuels in a range of reactors. The utilisation of CO₂ to several fuels and value-added chemical provides an attractive alternative to fossil fuels consumption. CO₂ 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 CO₂ 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 CO₂ conversions. Packed bed microreactors have been used for the production of hydrocarbons and methanol

- 981 from CO₂. A higher intensified process can be achieved by
 982 combining the benefits of a membrane with the advantages
 983 properties of a microreactor. The membrane microreactor can
 984 perform the hydrogenation reaction under milder conditions
 985 because of higher mass and heat transfer and requires lower
 986 catalyst quantities when compared to other conventional
 987 macroscopic reactors. Microwave and microplasma reactors
 988 offer a more novel approach to the traditional reactors
 989 discussed in this study. These microreactors can operate at
 990 significantly milder reaction conditions, as well as higher
 991 conversions. Future research can be directed towards
 992 investigating the hydrogenation of CO₂ for the production of a
 993 variety of fuels and chemicals. In addition, other microreactor
 994 configurations could be explored to understand and enhance
 995 the heterogeneous chemical reaction. This further research
 996 could make the replacement of conventional reactors with
 997 microreactors viable in the future. Lastly, further research
 998 should investigate the scalability of these microreactors to
 999 produce fuels on an industrial scale.
- 1000 **Conflicts of interest**
- 1001 There are no conflicts to declare.
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- 1003 There are no acknowledgments to declare.
- 1004 **References**
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