

Power to methanol

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Methanol is a very important raw material in chemical industry. As Fig. 5.1 shows, several other products can be obtained starting from methanol. It is also a very flexible liquid fuel as it can be used in spark-ignited internal combustion engines, pure or blended with gasoline and ethanol, as well as in fuel cells. Methanol exhibits favourable combustion properties and its combustion efficiency is higher than that of gasoline thanks to the higher octane number, whereas the lower heating value is about the half (Bromberg and Cheng, 2007). It is also safer and no more toxic than petroleum-based fuels and less dangerous in case of spill because it is water soluble and highly biodegradable (Malcolm Pirnie Inc. and American Methanol Institute, 1999).

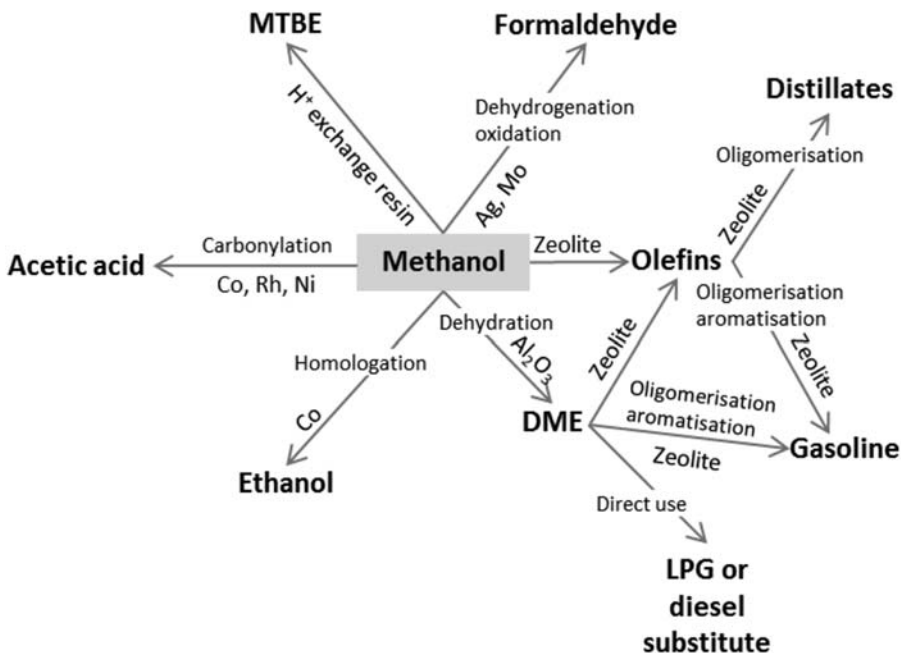


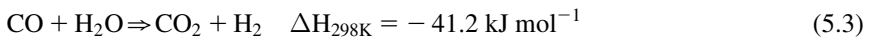
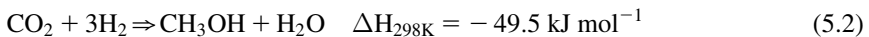
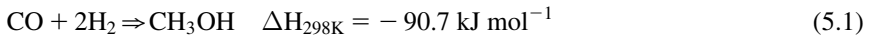
Figure 5.1 Main products obtainable from methanol (Bjorck, Dobson, and Pandhal, 2018).

Methanol production has always been based on synthesis gas obtained from fossil fuels via natural gas reforming or coal gasification; however, in the next future, renewable methanol can be produced starting from green hydrogen and biomass or captured CO₂.

5.1 Methanol production from syngas

The first process for industrial-scale synthesis of methanol dates back to one century ago. It operated at high pressures (250–350 bar) and temperatures (320°C–450°C) with a ZnO/Cr₂O₃ catalyst (Wender, 1996). That process was replaced about 60 years ago by a lower pressure (50–100 bar) and lower temperature (200°C–300°C) process with a copper-based catalyst (Studt et al., 2015; Supp, 1990). The commercially used catalysts for the synthesis of methanol are currently based on CuO and ZnO with the addition of some stabilizing elements such as Zr, Cr, Mg (Ali, Abdullah, and Mohamed, 2015; Jadhav et al., 2014; Wang et al., 2011).

The reactions involved in methanol synthesis are as follows:



The composition of a syngas, whether it is obtained from fossil fuels or biomass, has a hydrogen content that does not meet the stoichiometry required by methanol production, thus requiring an additional supply of hydrogen. This additional hydrogen can be derived from renewable energy sources through an electrolysis process and, therefore, it is globally a power to methanol process even in the case of fossil fuels as a carbon source. Obviously, starting from biomass, the produced methanol is totally renewable and the carbon dioxide emissions due to the final use of methanol are offset by the preventive carbon absorption by the biomass used.

Methanol synthesis is exothermic and is therefore favoured by low temperatures. Moreover, it involves a decrease in the number of moles and is therefore favoured by elevated pressures, according to Le Châtelier principle. This can be seen in Fig. 5.2 which shows the chemical equilibrium for reaction (5.1) and (5.2).

In the past, it was believed that the preferred carbon source for the production of methanol was carbon monoxide, while today it is believed that the main reaction is that of hydrogenation of carbon dioxide (Grabow and Mavrikakis, 2011; Lee et al., 1993). The reason why carbon dioxide hydrogenation experiments have given lower results than syngas hydrogenation (e.g. Pontzen et al., 2011) is that the production of water due to reaction (5.2) shifts the equilibrium of the reaction itself towards reactants and causes catalysts inactivation (Wu et al., 2001).

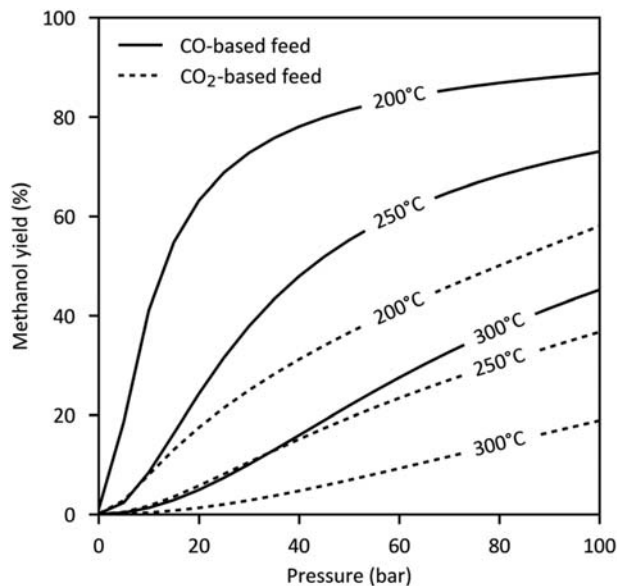


Figure 5.2 Equilibrium conversion of methanol formation (Dieterich et al., 2020).

Moreover, reaction (5.2) generates a lower amount of methanol at equilibrium. It is interesting to observe that when CO is used as a feed gas the activation energy of reaction (5.1) with a Cu catalyst is much lower than with a Cu/ZnO catalyst, whereas for a syngas the activation energy of reaction (5.2) with a Cu/ZnO is about a quarter lower than with a Cu catalyst, as shown in Fig. 5.3 (Studt et al., 2015). Moreover, the presence of carbon monoxide reduces the presence of water thanks to the water–gas shift reaction (5.3).

On the other hand, the reaction kinetics improves with higher temperatures at the expense of a lower final conversion. It is therefore necessary to recycle unconverted carbon oxides and hydrogen after cooling and steam condensation and separation (Fig. 5.4). Thanks to such a recycle, it is possible to obtain a very high conversion level, limited in practice only by the need to periodically purge the system to avoid the accumulation of unwanted substances contained into the fed gas or produced by competing reactions. To promote carbon conversion a slight excess of hydrogen can be used. This excess will be recycled as unreacted gas and therefore it is not lost, apart from a minimal amount with the purge gas.

Despite the elimination of unwanted substances by purging, the produced methanol is not entirely pure. According to the required purity, the produced methanol must therefore be subjected to a purification process. Dissolved gases are removed by flashing at a pressure between 5 and 10 bar. The next step is distillation, which can be carried out in a single column or in several columns depending on the purity required (Dieterich et al., 2020; Supp, 1990). A single column is suitable for fuel grade methanol, for which the water content is the only restriction, whereas higher

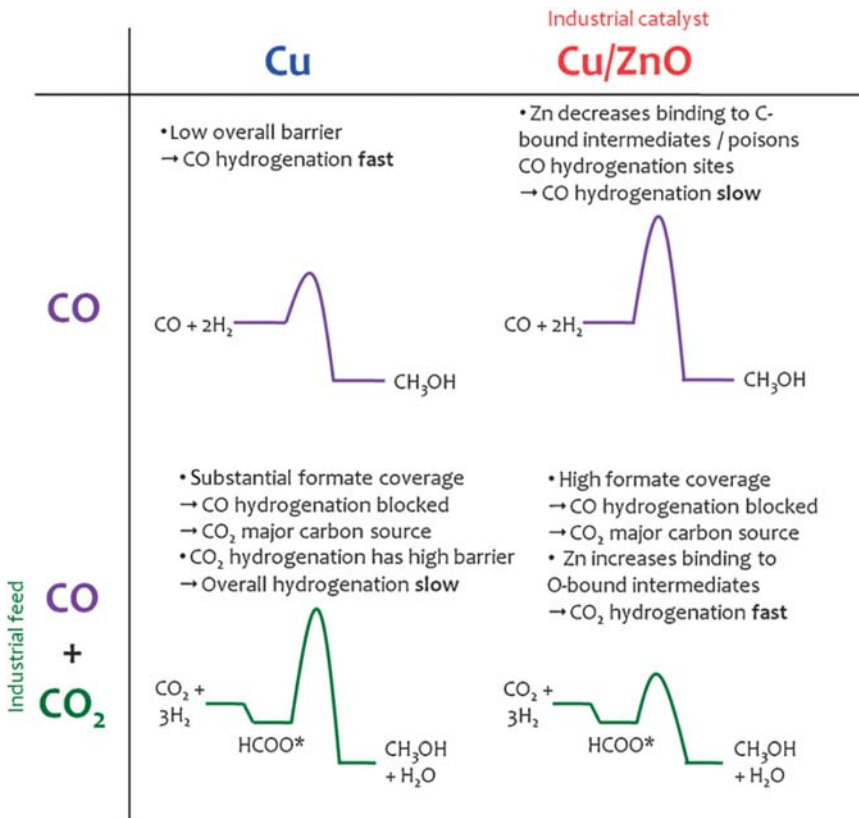


Figure 5.3 Energy barriers and activation energies in methanol synthesis reactions (Stude et al., 2015).

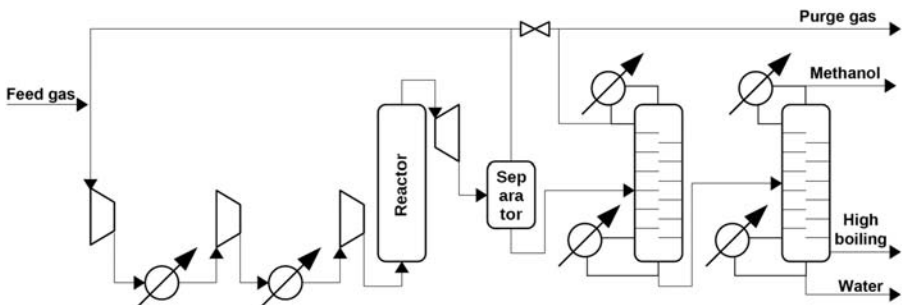


Figure 5.4 Flowsheet for a methanol production plant.

alcohols or liquid hydrocarbons do not pose problems. Commercial methanol is generally classified, according to the American Society for Testing and Materials, in A and AA purity grades (ASTM, 2012). Chemical methanol is normally grade AA. Two distillation columns are required for grade A methanol and three or four distillation columns are required for grade AA methanol (Andika et al., 2018).

In the case of a single column the high-boiling products and the process water are extracted from the bottom of the column, while liquid methanol and low-boiling products in the gaseous state are extracted from the top. In the case of two columns the first separates the low-boiling products, while the second separates methanol from the high-boiling products (Supp, 1990).

The selectivity of currently used catalysts is very high, over 99% (Twigg and Spencer, 2001). The impurities present in the final product [e.g. ethanol, methyl formate, dimethyl ether (DME), acetone] are thermodynamically favoured with respect to methanol. The formation of these by-products is favoured by the impurities of the catalyst, by high pressures and by the strong presence of carbon monoxide compared to the other reactants (Dieterich et al., 2020; Hansen and Nielsen, 2008).

The catalyst can be deactivated by poisoning or sintering (Fig. 5.5), and however, a duration of more than 4 years was demonstrated (Filippi and Badano, 2007; Hirotani, Nakamura, and Shoji, 1998). Impurities are usually eliminated upstream of the process until the typical purity requirements for the supply gas are met (Table 5.1). The compounds of sulphur and, above all, of chlorine are the most harmful. Sulphur can be eliminated thanks to the zinc oxide present in the catalysts (Kung, 1992).

Guard beds can be provided to protect the catalyst. The guard bed can be placed in a separate reactor or in the same reactor as the catalyst, obviously upstream of the catalysis bed. This guard bed can be constituted by alkalis alumina or by the catalyst itself (Moreo, 2011; Nielsen, 2009; Twigg and Spencer, 2001). It follows that sintering remains the only real cause of catalyst deactivation.

Compared to past ones, modern catalysts show a longer useful life and are able to maintain higher activity and selectivity even at the end of their life. For instance, Haldor Topsøe reported noticeable catalyst improvements in moving from MK-101,

Table 5.1 Gas purity requirements for Cu/ZnO based catalysts (Dieterich et al., 2020).

Component	Purity required
H ₂ S	<0.05 ppm
HCl	1 ppb
Metal carbonyl	Few ppb
Particles	<0.1 mg Nm ⁻³
Tar	<1.0 mg Nm ⁻³
Alkalis	<0.25 mg Nm ⁻³

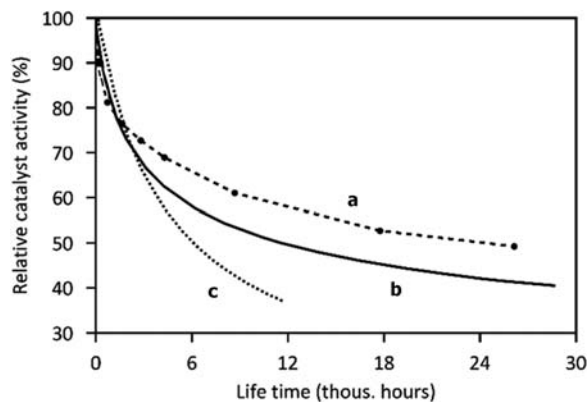


Figure 5.5 Deactivation curves of commercial methanol catalysts: (a) typical deactivation curve, (b) deactivation model fitted to a 295 t day^{-1} Lurgi plant, (c) Haldor Topsøe MK-101, industrial plant.

Source: Adapted from Dieterich, V. et al. (2020). Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: A review. *Energy and Environmental Science*, 13(10), 3207–3252. <https://doi.org/10.1039/d0ee01187h>.

to MK-121, to their recent product MK-151 Fence (Hansen, 2015; Nielsen, 2009). In general, a reduction of the catalyst activity over time is however inevitable.

To maintain a constant production of methanol along the time, the operating temperature can be gradually increased (Heydorn, Diamond, and Lilly, 2003).

Obviously, an important aspect in the development of this technology is that of costs and, consequently, of the economy of scale. Going from a capacity of 2000 t day^{-1} to 5000 t day^{-1} , the plant cost increases by only 75%, whereas a $10,000 \text{ t day}^{-1}$ plant costs only about the triple (Dieterich et al., 2020).

Reactor employed for methanol synthesis is similar to those utilised for Fischer–Tropsch and DME synthesis and can be classified in three different categories: fixed bed reactors (FBRs), fluidised bed reactors and liquid-phase reactors (Table 5.2). There are different FBR types:

- adiabatic, which requires a series of reactors with an intercooling system to keep the temperature at a proper level;
- polytropic
 - quench, which requires two separate bed sections and injection of cold feed reactant gas in between and
 - gas-cooled converter, in which cold gas refrigerates the catalyst; and
- steam raising converter (SRC), in which water evaporates on the opposite side of the catalyst.

Fluidised bed reactors and liquid-phase reactors are both isothermal. Fluidised bed reactors have not yet reached a commercial level, while among the liquid-phase reactors, only one has been industrialised. There are other alternative concepts as

Table 5.2 Kinds of reactors for methanol synthesis (Dieterich et al., 2020).

	FBR				Fluidised bed reactor	Liquid-phase reactor
	Adiabatic FBR	Quench	SRC	GCC		
Operation mode	Adiabatic	Polytropic	Isothermal	Polytropic	Isothermal	Isothermal
State of catalyst	Catalyst bed	Catalyst bed divided into sections	Catalyst filled into shell or tube side	Catalyst filled into shell or tube side	Catalyst in fluidised bed	Catalyst suspended in liquid hydrocarbons
Cooling concept	Series of reactors with intercooling	Cold feed gas is injected between sections	Cooled by water evaporation on opposing side of the catalyst	Cooled by preheating cold gas passing through the catalyst bed in tubes	Submerged coil heat exchanger	Liquid hydrocarbons as heat transfer medium; heat removed in internal heat exchanger
Advantages	Simple scale-up, no mechanical stress of catalyst, defined residence time	No mechanical stress of catalyst, improved temperature control	Very efficient heat recovery, good heat transfer and temperature control		High heat transfer coefficients, uniform temperature distribution	Excellent heat transfer performance, isothermal reaction profile
Disadvantages	Lower heat transfer, danger of hotspots, several pressure vessels and piping	Large catalyst volume	Large number of tubes, expensive	Limited heat transfer	Nonuniform residence time (bubble formation), attrition of catalyst, erosion of internals, difficult scale-up	High mechanical stress of catalyst

FBR, Fixed bed reactor; GCC, gas-cooled converter; SRC, steam raising converter.

well, such as membrane reactors, drip bed reactors and suspension reactors, but all require further development (Dieterich et al., 2020).

The most common reactor is nowadays the steam raising FBRs (or SRC) which is quasiisothermal (see Fig. 5.6) thanks to the heat removed by the water evaporation.

Fig. 5.7 shows several kinds of commercial reactors:

1. Lurgi tubular reactor, in which the gas flows inside a series of tubes containing the catalyst, whereas the boiling water is outside, in the vessel, generating medium pressure steam.
2. Linde Variobar, in which the boiling water circulates inside a coil, while the catalyst is distributed outside.
3. Toyo Multistage Radial Flow, which is a reactor developed in collaboration by Toyo Engineering Corporation and Mitsui Toatso Chemicals and differs from the previous two for the gas flow, which is radially distributed from the outside and is collected centrally after passing through the catalytic bed; cooling is achieved by means of coaxial pipes with water supply from the inside and steam production in the external annular section.
4. Mitsubishi Superconverter, which was developed in collaboration by Mitsubishi Gas Chemical and Mitsubishi Heavy Industries. Also, this reactor has a series of coaxial tubes, but they are crossed by the gas which preheats through the inner tube and then reacts by crossing the catalyst in the outer annular section; the cooling water is contained in the external vessel as in the Lurgi tubular reactor.
5. Methanol Casale isothermal methanol converter (IMC), which is characterised by the presence of hollow plates inside the catalysis bed; the bed is cooled by the circulation of a fluid inside the plates even with different flow rates at different heights, to maintain an almost isothermal temperature profile; the refrigerant fluid can be either the supply gas itself or boiling water.

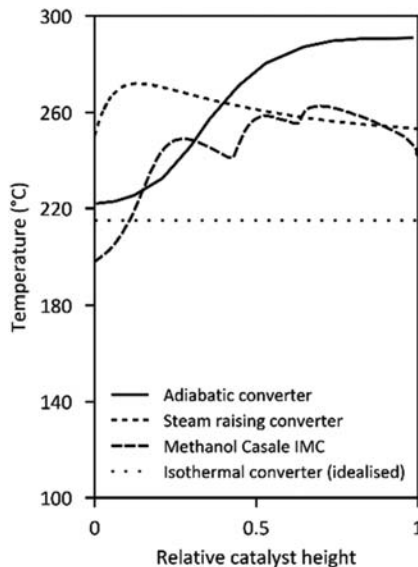


Figure 5.6 Temperature profiles along the reactor length of some reactors (Dieterich et al., 2020).

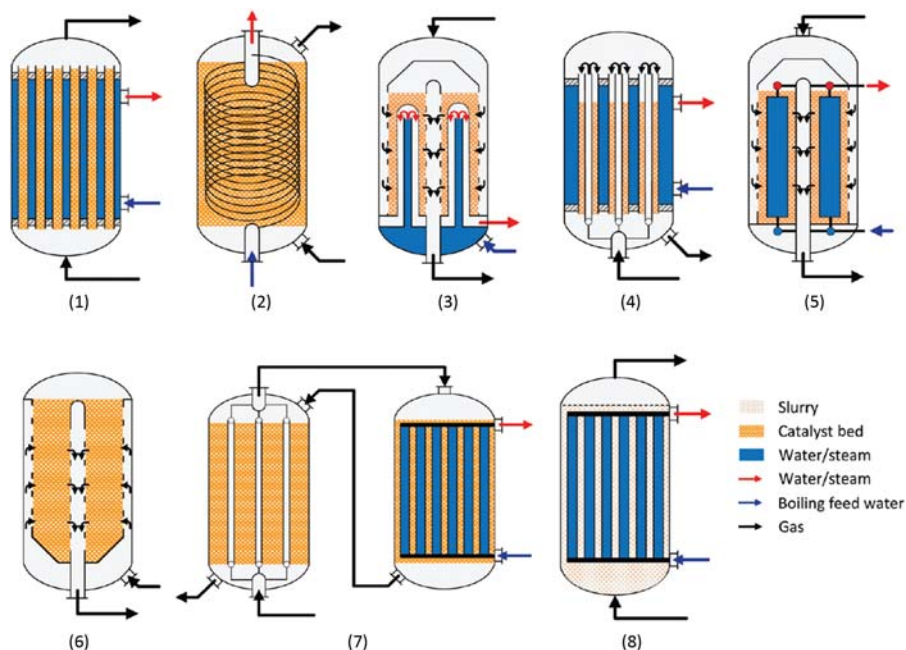


Figure 5.7 Simplified reactor layouts (Dieterich et al., 2020).

6. Haldor Topsøe adiabatic reactor, which is a multistage adiabatic reactor with intercooling.
7. Lurgi MegaMethanol, which is a two-stage reactor consisting of a first bed cooled with boiling water and a second bed cooled with the feed gas that is thus preheated.
8. Air Products LPMcOH (liquid-phase methanol), which, unlike the others, is not a FBR but formed by a mineral oil in which the catalyst particles are suspended; this solution achieves an excellent heat transfer, but at the expense of a low catalyst density inside the bed.

Several data about these kinds of reactors are shown in [Tables 5.3](#) and [5.4](#) in which they are respectively grouped on the basis of gas flow direction: axial or radial and axial-radial (for Methanol Casale IMC). This is an important difference since it affects the pressure drop, which is significantly lower for radial flow reactors. As a consequence, also the power needed for recycled gas recompression is lower for radial flow reactors. Moreover, for the same reason, radial flow reactor could be higher than axial flow one.

As previously mentioned, reactions that lead to the production of methanol are exothermic and therefore favoured by low temperature which, on the other hand, is unfavourable in terms of the efficiency of the process. The high temperatures therefore speed up the process, but the final carbon conversion is lower.

Therefore the reactor design is important not only for its ability to retain temperature within the ideal range for reactions but also for the efficiency of recovery of the generated heat. In general, higher outlet/peak temperature allows to produce steam at higher pressure. For most industrial reactors in operation the ranges of

Table 5.3 Characteristics and operating parameters of main commercial axial flow reactors.

	Lurgi	Superconverter	MegaMethanol	LPMeOH
Licensors	Lurgi	MGC and MHI	Lurgi	Air products
Type	SRC	GCC/SRC	GCC and SRC	Slurry
Catalyst location	Tube side	Double pipes	Shell side	Shell side
Heat exchanger	Tubular	Tubular	Tubular	Tubular
Stages	1	1	2	1
T _{out} (°C)	255	190	220	215
T _{peak} (°C)	270	270	270	215
Pressure (bar)	50–100	55–100	75	30–50
Recycle ratio	3–4	2–3	2–2.7	1–5
MeOH yield (mol%)	6–7	10–15	11	8–12
Max capacity (t day ⁻¹)	1500–2200	Not available	5000–10,000	Low
Steam pressure (bar)	29–43	19–45	50–60	16–25
Plants/projects	>55	9	>10	Demo

GCC, Gas-cooled converter; MGC, Mitsubishi gas chemical; MHI, Mitsubishi heavy industries; SRC, steam raising converter.

Source: Adapted from Dieterich, V. et al. (2020). Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch fuels: A review. *Energy and Environmental Science*, 13(10), 3207–3252. <https://doi.org/10.1039/d0ee01187h>.

operating temperatures and pressures are, respectively, 200°C–300°C and 50–100 bar, while the pressure range for the steam obtained is 16–45 bar, with the sole exception of the Lurgi which allows to obtain steam between 50 and 60 bar (see Table 5.3).

Another parameter that differentiates the reactor types is the recycle factor (f_r) required to obtain high overall conversion values:

$$f_r = \frac{F_{V,rg}}{F_{V,fg}} \quad (5.4)$$

with $F_{V,rg}$ and $F_{V,fg}$ representing the volumetric flow of recycled gas and feed gas, respectively.

Table 5.4 Characteristics and operating parameters of main commercial radial flow reactors.

	IMC	Variobar	MRF-Z	Haldor Topsøe
Licensor	Methanol Casale	Linde	Toyo (TEC)	Haldor Topsøe
Type	SRC	SRC	SRC	Adiabatic
Catalyst location	Shell side	Shell side	Shell side	Fixed bed
Heat exchanger	Plate	Tubular	Bayonet	Intercooler
Stages	1	1	1	2–4
T _{out} (°C)	225	Not available	240	290
T _{peak} (°C)	280	Not available	280	Not available
Pressure (bar)	65–80	50–150	80–100	50–100
Recycle ratio	3	Not available	Not available	3–5
MeOH yield (mol%)	10.1–13.3	Not available	10	7
Max capacity (t day ⁻¹)	7000–10,000	4000	5000	10,000
Steam pressure (bar)	25–32	40	Not available	Not available
Plants/projects	9	8	6	>40

IMC, Isothermal methanol converter; SRC, steam raising converter.

Source: Adapted from Dieterich, V. et al. (2020). Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: A review. *Energy and Environmental Science*, 13(10), 3207–3252. <https://doi.org/10.1039/d0ee01187h>.

As already written, a total conversion is not possible due to the need for purge. As the conversion increases in the single passage inside the reactor, the recycle factor decreases: Table 5.3 shows f_r values ranging from a minimum of 1 to a maximum of 5 and allow to obtain a carbon conversion in a range of 93%–98%. Reducing the amount of recycled gas makes it possible to adopt a smaller reactor and to consume less energy for gas recompression.

When the conversion is carried out in more than one stage, it is possible to condense and separate the methanol between one stage and the other, thus favouring the conversion in the next stage and reducing the final amount of unreacted gas.

This can be done for adiabatic reactors, while among SRCs, only the Lurgi MegaMethanol features a double stage (Bertau et al., 2014).

A parameter used to normalise the gas flow to the reactor size is the gas hourly space velocity (GHSV):

$$\text{GHSV} = \frac{F_{V,g,\text{in}}}{V_R} \quad (5.5)$$

where $F_{V,g,\text{in}}$ is the volumetric flow in standard condition of the feed gas and V_R is the volume of the reactor. In the case of SRCs, its value ranges from about 6000 to 12,000 h^{-1} for each stage, whereas LPMeOH shows GHSV lower than 5000 h^{-1} (Dieterich et al., 2020).

Other types of reactors have been developed but have not been built on an industrial scale (Arora et al., 2018; Gallucci and Basile, 2007; Pass et al., 1990; Rahimpour and Ghader, 2003; Terreni et al., 2019).

5.2 Methanol production from carbon dioxide

As can be seen from the comparison between reactions (5.1) and (5.2), this second reaction is less favourable because it requires an extra mole of hydrogen for each mole of methanol obtained. However, the methanol production starting from carbon dioxide is interesting today because it is connected to the possibility of reducing climate-altering gases emissions into the atmosphere by capturing the carbon dioxide directly from the sources with the greatest concentration (chimneys of power plants and industries).

Although catalysts similar to those for syngas conversion have been used (Doss, Ramos, and Atkins, 2009; Pontzen et al., 2011), these are not ideal for this process. In fact, in this case the presence of water in the reactor is much greater (30%–40% vs 10%–15% for production from syngas) and, since it is also a product, it hinders the progress of the reaction. Against this disadvantage, carbon dioxide production offers a much lower by-product content (see Table 5.5) and a lower consumption for methanol distillation as a consequence.

Due to the large water production, it is necessary to develop specific catalysts. Information on these new catalysts can be found in two recent reviews (Dang et al., 2019; Guil-López et al., 2019).

The study and application of specific catalysts for the production of methanol starting from carbon dioxide began in the 1990s. Examples and information on both such catalysts and reactors are reported by Dieterich et al. (2020). They are mostly small fixed bed pilot reactors, with only three of them exceeding 100 t year^{-1} . The temperatures are all around 250°C, whereas the pressures have a much wider range, between 30 and 100 bar. The GHSV and the conversion rate are also very variable, respectively, from 1 to 18 h^{-1} and from 40% to 96.5% (the latter obtained thanks to a two-stage process).

Table 5.5 Raw methanol compositions of CO and CO₂-based feed gas.

	CO-syngas	CO ₂ -based feed gas (H ₂ :CO ₂ = 3)
Temperature (°C)	250	230–270
Main components (wt%)		
Methanol	84.5	63.0–63.7
Water	15.4	35.6–36.9
Impurities (wt ppm)		
<i>n</i> -Paraffins	78	0
Higher alcohols	626	28–148
Esters (mainly methyl formate)	582	129–450
Ketones	24	0
Dimethyl ether	61	14–24
Total impurities (wt ppm)	1371	248–478
Methanol selectivity, except water (%)	99.84	99.92–99.96

Source: Adapted from Dieterich, V. et al. (2020). Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: A review. *Energy and Environmental Science*, 13(10), 3207–3252. <https://doi.org/10.1039/d0ee01187h>.

5.3 Innovative processes

Alternative processes to thermochemical synthesis are also being studied:

- electrochemical conversion (coelectrolysis);
- biological conversion; and
- photocatalytic conversion, in which photosynthesis is emulated to perform the reduction of carbon dioxide thanks to sunlight and suitable catalysts and produce synthetic fuels.

Obviously, they have not yet reached technical maturity and economic convenience. Moreover, photocatalytic conversion could store solar energy but is not a power to fuel technology and will be not considered.

5.3.1 Coelectrolysis

An interesting alternative process which is gaining increasing interest is coelectrolysis.

A coelectrolyser (Fig. 5.8) is a solid oxide electrolyser fed with steam and carbon dioxide at the cathode where H₂O and CO₂ reduction reactions (5.6) and (5.7) occur together with reaction (5.3):



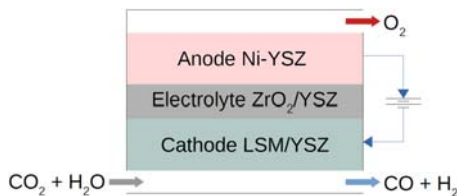


Figure 5.8 Coelectrolyser.

The oxygen evolution reaction takes place at the anode:



The most common electrolyte is a ceramic layer of ZrO_2 doped with Y_2O_3 (YSZ, yttria-stabilized zirconia), stable and capable to conduct ions at high temperatures (800°C – 1000°C). The most common materials used for electrodes are lanthanum strontium manganite/YSZ for anode and nickel–YSZ for cathode.

The direct electrochemical reduction of carbon dioxide to methanol was tried by some researchers along the last decades. Semiconductor electrodes were tested by Freese and Leach with the goal to store solar energy in methanol: GaAs and InP showed a good selectivity but required a high potential and suffered from corrosion (Canfield and Freese, 1983). Subsequent experiments with metal electrodes such as Pd, Pt, Co and Fe did not give good results because the main product was carbon monoxide. Using molybdenum electrodes, methanol can be obtained as the major carbon-containing product with small amounts of carbon monoxide and traces of methane (Summers, Leach, and Freese, 1986). Cu-based catalysts, in particular Cu/ZnO, appear more promising for the conversion of CO_2 and CO to methanol in the presence of H_2 (Freese, 1991). Ruthenium was also tested with some good results (Popić, Avramov-Ivić, and Vuković, 1997; Spataru et al., 2003).

However, the current technology is cost competitive only for carbon monoxide production (Durst et al., 2015) so that it is necessary for a subsequent synthesis process to obtain methanol.

5.3.2 Biological oxidation of methane

There is not a direct biological conversion from carbon dioxide to methanol, but methanol could be obtained from methane. Therefore a two-step process from power to methane and methane to methanol can be considered when the desired final product is a liquid fuel.

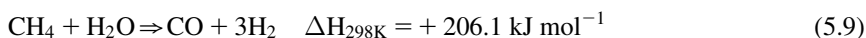
Just as methanogenic bacteria exist, there are many others (methanotrophic) which feed on methane and are capable to generate methanol as an intermediate compound in their metabolism. Methanogenic bacteria live in swamps, rivers,

oceans, ponds and sewage sludge producing methane through the anaerobic decay of organic matter. Therefore most methanotrophic bacteria live in the same environments, exploiting the oxygen of other compounds, or at the aerobic–anaerobic interface by oxidising the methane produced by the former. They are also mesophilic bacteria too, but they adapt well to other temperatures.

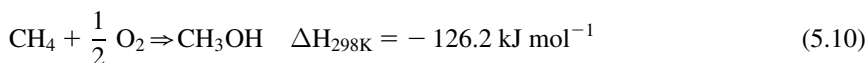
Biological methanol production is catalysed by methane monooxygenase (MMO) enzymes in a single step at atmospheric pressure, 25°C–35°C, and pH in the range 7.0–7.65 (Hanson and Hanson, 1996). Methanotrophic bacteria metabolism is more complex and also based on other enzymes: methanol dehydrogenase (MDH), formaldehyde dehydrogenase (FADH) and formate dehydrogenase (FDH). The chain of subsequent transformations is represented in Fig. 5.9. The methanol produced by MMO is sequentially converted to formaldehyde by MDH, to formate by FADH and finally to carbon dioxide by FDH.

In the initial reaction the MMO breaks the O–O bond of the oxygen molecule using substances that change from the reduced to the oxidised form (e.g. NADH → NAD⁺). One of the oxygen atoms binds to the methane molecule to generate methanol, while the other oxygen atom combines with hydrogen and produces water (Lipscomb, 1994).

It could be a valid alternative to the traditional conversion from methane to methanol, which is an energy-intensive and expensive process because it requires high temperatures and pressures. Whereas the commercial process proceeds in two steps, namely methane reforming (5.9), highly endothermic:



followed by methanol synthesis (5.1), the direct conversion from methane to methanol is an exothermic reaction:



Another advantage is that this process is suitable for small-scale operations, that is connected to a distributed production of methane, and requires a low investment. Unfortunately, the transition from laboratory experiments to industrialisation of the process requires, as always, the overcoming of some obstacles.

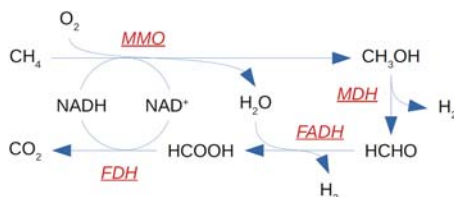


Figure 5.9 Simplified pathway for oxidation of methane in methanotrophic bacteria.

The main options for achieving the partial oxidation of methane to methanol using the knowledge developed about the enzyme MMO are the following:

- whole-cell methanotrophic culture
- genetically modified organisms
- isolated MMO enzymes
- synthetic MMO analogues
- ammonia oxidising bacteria

The direct culture of methanotrophic bacteria is certainly the cheapest solution since the bacteria themselves take care of all the biological apparatus necessary for the process as well as their own reproduction. However, it is evident that the metabolism of whole cells is not devoted to the production of methanol and therefore problems arise related to the interruption of the natural process which is feasible by inhibition of the MDH enzyme. Furthermore, a splitting of the process must be provided in a methanol production section and a mother culture section intended for cell reproduction.

An alternative is to try to optimise the reaction processes using whole cells by genetic engineering. However, in this sector, we are still at the patent level (e.g. [Silverman and Regitsky, 2014](#)) without applications that can demonstrate its feasibility.

The only component of methanotrophic bacteria useful for the conversion of methane to methanol is the MMO enzyme. Therefore it is possible to think of using it in isolation, immobilised on artificial matrices, thus avoiding the other reactions of the metabolism of these bacteria. The advantage of avoiding unnecessary reactions is contrasted by the need to isolate and purify the enzyme ([Hakemian and Rosenzweig, 2007](#)) and, ultimately, the activity and duration that impact on the operating cost and do not make this option currently advantageous over whole-cell culture.

Wanting to overcome these limits, one could resort to the creation of catalysts that emulate the behaviour of MMO enzymes, to obtain a stable thermochemical process aimed only at the production of methanol. This is an option that could also bring other advantages in terms of optimisation (selectivity, efficiency and speed of conversion), even if it is still an immature technology ([Que and Tolman, 2008](#)).

Even the bacteria that oxidise ammonia, through the enzyme ammonia monooxygenase, are able to oxidise methane to form methanol ([Hyman, Murton, and Arp, 1988](#); [Taher and Chandran, 2013](#)), but also in this case the technology is not yet mature.

Nomenclature

F	flow in standard condition
f	factor
FADH	formaldehyde dehydrogenase
FBR	fixed bed reactor

FDH	formate dehydrogenase
GCC	gas-cooled converter
GHSV	gas hourly space velocity
LSM	lanthanum strontium manganite
MDH	methanol dehydrogenase
MMO	methane monooxygenase
NAD	nicotinamide adenine dinucleotide
SRC	steam raising converter
V	volume
YSZ	yttria-stabilized zirconia

Subscripts

f	feed
g	gas
R	reactor
r	recycled
V	volumetric

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