# Methanol

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**Abbreviations used in this article:**

ATR:       autothermal reformer
CTF:       covalent triazine-based framework
DICP:      Dalian Institute of Chemical Physics
DME:       dimethyl ether
DMT:       dimethyl terephthalate
DMTO:      DICP methanol-to-olefins
ETBE:      ethyl *tert*-butyl ether
FAMEs:     fatty acid methyl esters
HP:        high-pressure
LP:        low-pressure
LPMEOH:    liquid phase methanol

MP:          medium-pressure
MTA:         methanol-to-aromatic compounds
MTBE:        methyl *tert*-butyl ether
MTG:         methanol-to-gasoline
MTO:         methanol-to-olefine
MTP:         methanol-to-propene
MUG:         make-up gas
RVP:         Reid vapor pressure
RWGS:        reverse water–gas shift
SRK:         Soave–Redlich–Kwong

## 1. Introduction

Methanol [67-56-1], $CH_3OH$, $M_r$ 32.042, also termed methyl alcohol or carbinol, is one of the most important chemical raw materials. About 85% of the methanol produced is used in the chemical industry as a starting material or solvent for synthesis. The remainder is used in the fuel and energy sector; this use is increasing. Worldwide production capacity in 1989 was ca. $21 \times 10^6$ t/a. In 1993, worldwide production capacity amounted to $22.4 \times 10^6$ t/a. In 2011, the consumption of pure methanol reached almost $47 \times 10^6$ t/a; the major part is used in the formaldehyde industry followed by the acetic acid industry [1].

**Historical Aspects.** Methanol was first obtained in 1661 by Sir ROBERT BOYLE through the rectification of crude wood vinegar over milk of lime. He named the new compound *adiaphorus spiritus lignorum*. JUSTUS VON LIEBIG (1803–1873) and J. B. A. DUMAS (1800–1884) independently determined the composition of methanol. In 1835, the term "methyl" was introduced into chemistry on the basis of their work.

From ca. 1830 to 1923, "wood alcohol", obtained by the dry distillation of wood, remained the only important source of methanol. As early as 1913, A. MITTASCH and coworkers at BASF successfully produced organic compounds containing oxygen, including methanol, from carbon monoxide and hydrogen in the presence of iron oxide catalysts during developmental work on the synthesis of ammonia. The decisive step in the large-scale industrial production of methanol was made by M. PIER and coworkers in the early 1920s with the development of a sulfur-resistant zinc oxide–chromium oxide ($ZnO$–$Cr_2O_3$) catalyst. By the end of 1923, the process had been converted from the developmental to the production stage at the BASF Leuna Works.

The processes were performed at high pressure (25–35 MPa) and 320–450 °C. They dictated the industrial production of methanol for more than 40 years. In the 1960s, however, ICI developed a route for methanol synthesis in which sulfur-free synthesis gas containing a high proportion of carbon dioxide was reacted on highly selective copper oxide catalysts. This and other related low-pressure processes are characterized by fairly mild reaction conditions (5–10 MPa, 200–300 °C). Today's industrial methanol production is still based on these principles. However, the capacity of large-scale plants has increased to more than 5 000 t/d.

## 2. Physical Properties

At ambient conditions, methanol is a liquid with relatively high polarity and medium vapor pressure. It is colorless and can be used as a typical organic solvent being able to dissolve substances with high and medium polarity [2, 3]. It is miscible with water, alcohols, various organic solvents, and to a limited extend with oils and fats. It is a well-known chemical and its chemical properties can be found in literature in detail. A selection of the key physical data is shown in Table 1.

More detailed information about pure methanol and its mixtures can be found in literature, e.g., solvent properties [6, 7], temperature-dependent properties [9], thermodynamic data [10], liquid heat capacity and enthalpy [11], viscosity [9, 12–17], conductivities [21–23], and safety aspects [21, 22].

## 3. Chemical Properties

Methanol is the simplest aliphatic alcohol. As a typical representative of this class of substances, its reactivity is determined by the functional hydroxyl group [23–25]. Reactions of methanol take place via cleavage of the C—O or O—H bond and are characterized by substitution

**Table 1.** Selection of physical data of methanol

| Property | Value | Conditions | Reference |
|---|---|---|---|
| Molar mass, g/mol | 32.042 | | |
| Density, kg/m$^3$ | 786.68 | 298.15 K | [4] |
| $T_{bp}$, K | 337.8 | ambient | [5] |
| $T_{mp}$, K | 175.27 | | [4] |
| Viscosity, mPas | 0.5513 | 298 K, liquid | [6, 7] |
| $T_{crit}$, K | 513 | | [5] |
| $p_{crit}$, MPa | 8.1 | | [5] |
| $\rho_{crit}$, mol/L | 8.51 | | [5] |
| $V_{crit}$, cm$^3$/mol | 116 | | [5] |
| $\Delta H_f^0$, kJ/mol | −205 | 273.15 K, 101.3 kpa | [8] |
| $C_p$, J mol$^{-1}$ K$^{-1}$ | 42.59 | 273.15 K, 1 bar, gas | [8] |
| | 80.9 | 298.15 K, 101.3 kpa, liquid | |
| Thermal conductivity, mW m$^{-1}$ K$^{-1}$ | 190.16 | 298.15 K, liquid | [6, 7] |
| Dielectric constant | 32.65 | 298.15 K | [6, 7] |
| Flash point, K | 288.75 | DIN 51 755 | [4] |
| Ignition temperature, K | 743.15 | DIN 51 794 | [4] |
| Explosion limits, vol% | 6.72–36.50 | | [4] |
| Explosion group | II B, T1 | | |
| Heating value, MJ/kg | 22.693 | 298.15 K | [4] |
| Antoine equation parameters | $\log(p) = 5.15853–(1569.613/(T–34.846))$ | 353.4–512.63 K | [5] |
| | $2\log(p) = 5.20409–(1581.341/(T–33.50))$ | 288.0–356.83 K | |

of the −H or −OH group (→ Alcohols, Aliphatic) [26]. In contrast to higher aliphatic alcohols, however, $\beta$-elimination with the formation of a multiple bond cannot occur.

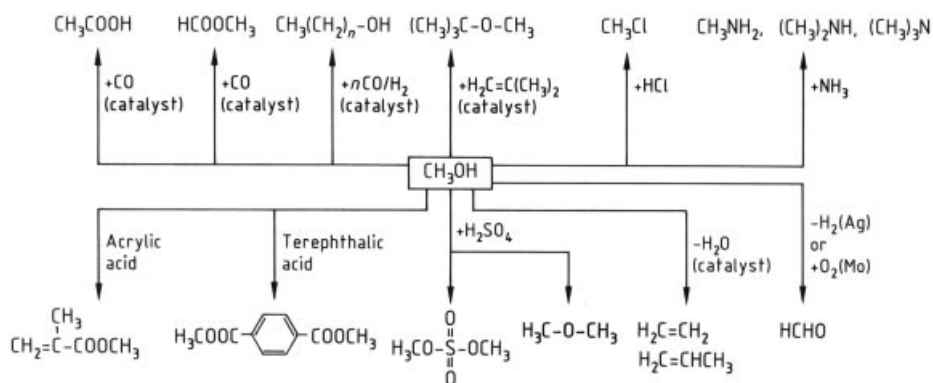Important industrial reactions of methanol include the following (Fig. 1):

- Dehydrogenation and oxidative dehydrogenation
- Carbonylation
- Esterification with organic or inorganic acids and acid derivatives
- Etherification
- Addition to unsaturated bonds
- Replacement of hydroxyl groups

# 4. Production

## 4.1. Principles

### 4.1.1. Thermodynamics

The formation of methanol from synthesis gas containing both carbon monoxide (CO) and carbon dioxide ($CO_2$) can be described by the following equilibrium reactions:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H_{300\,K} = -90.77\,\text{kJ/mol} \tag{1}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H_{300\,K} = -49.16\,\text{kJ/mol} \tag{2}$$
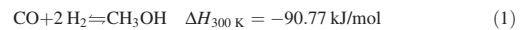


**Figure 1.** Industrially important reactions of methanol

Reaction enthalpies are determined from the standard enthalpies of the reactants and products [27]. Both reactions are exothermic and accompanied by a decrease in volume. Methanol formation is therefore favored by increasing pressure and decreasing temperature, the maximum conversion being determined by the equilibrium composition.

In addition to the two methanol-forming reactions, the endothermic reaction of carbon dioxide and hydrogen (Eq. 3, the reverse water–gas shift reaction, RWGS) must also be taken into account:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_{300\,K} = 41.21\ kJ/mol \qquad (3)$$
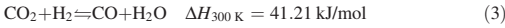
For the sake of simplicity, Equations (1) and (3) can be discussed as independent reaction pathways. The conversion of $CO_2$ to methanol (Eq. 2) is then the overall result of Equations (1) and (3), and the equilibrium constant $K_2$ can be described as $K_2 = K_1 \times K_3$. When the nonideal behavior of gases is taken into account, the equilibrium constants are determined as follows:

$$K_1 = \left[\frac{f_{CH_3OH}}{f_{CO}f_{H_2}^2}\right] = \left[\frac{\varphi_{CH_3OH}}{\varphi_{CO}\varphi_{H_2}^2}\right]\left[\frac{p_{CH_3OH}}{p_{CO}p_{H_2}^2}\right] = K_\varphi 1 \cdot K_{p1}$$

$$K_3 = \left[\frac{f_{CO}f_{H_2O}}{f_{CO_2}f_{H_2}}\right] = \left[\frac{\varphi_{CO}\varphi_{H_2O}}{\varphi_{CO_2}\varphi_{H_2}}\right]\left[\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}}\right] = K_\varphi 3 \cdot K_{p3}$$

where $f_i$ is the fugacity, $\varphi_i$ the fugacity coefficient, and $p_i$ the partial pressure of the $i$-th component.

There are a number of numerical formulations for calculating the temperature-dependent equilibrium constants $K_1$ [28–35] and $K_3$ [33–36]; their results differ widely [37]. A standard model extensively used for process simulations was given by GRAAF in 1986 [33].

$$K_1 = 10^{\left(\frac{5139}{T} - 12.621\right)}$$

$$K_2 = 10^{\left(\frac{3066}{T} - 10.592\right)}$$

$$K_3 = 10^{\left(\frac{-2073}{T} + 2.029\right)}$$

The fugacity coefficients can be determined according to [38] by assuming ideal solubility for the individual pure components, or they can be calculated from suitable equations of state [39, 40].

The equilibrium conversions can be calculated using a suitable equation of state model, e.g., the Soave–Redlich–Kwong model (SRK). For a standard synthesis gas containing CO, $CO_2$, and inerts (15 vol% CO, 8 vol% $CO_2$, 74 vol% $H_2$, and 3 vol% $CH_4$) the equilibrium conversions at different conditions are shown in Figure 2. At high temperatures, the methanol formation reactions are not favored and the RWGS reaction is dominant, as indicated by a net CO formation from $CO_2$.

### 4.1.2. Kinetics and Mechanism

Although constantly under investigation since the beginning of methanol research, the exact
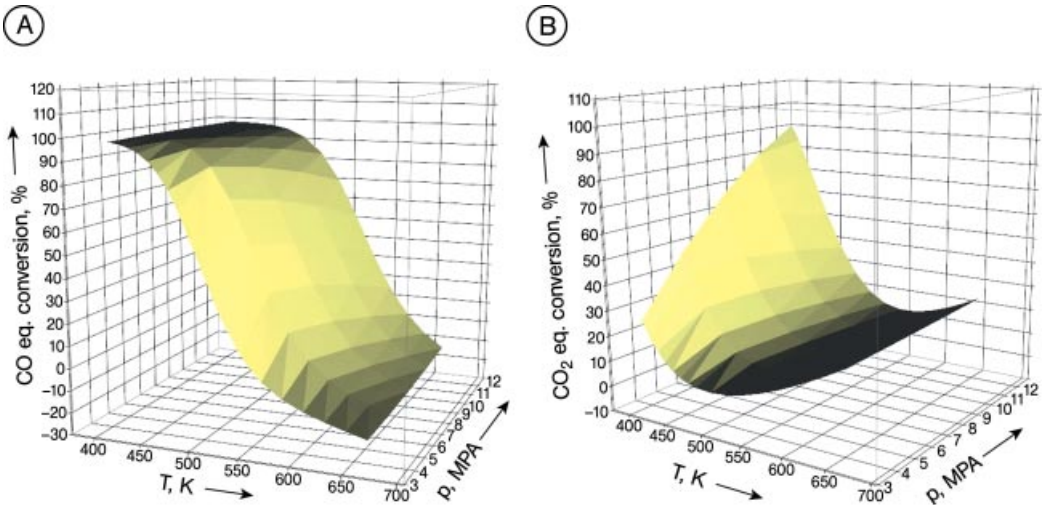
**Figure 2.** Dependence of reaction equilibrium on pressure and temperature on A) CO conversion and B) $CO_2$ conversion

mechanism is still discussed in academia and industrial research. The catalyst system used in industry is based on Cu–ZnO–Al$_2$O$_3$. Each of the elements is considered essential for the overall catalyst performance, i.e., activity, selectivity, and stability. The Cu-centers are generally regarded as main active sites, as indicated by a dependence of activity on the Cu surface area [41]. The presence of ZnO is thought to have a stabilizing effect on Cu(I) [42]. Al$_2$O$_3$ (or Cr$_2$O$_3$ as alternative) stabilizes and prevents sintering of the active particles [48, 43]. In addition, the mixed oxide nature of the catalyst leads to an increase of surface defects that are responsible for increased catalyst activity.

The influence of the CO$_2$ content on the reaction kinetics has been discussed controversially since the 1980s [37, 44–47]. Whereas some authors find a sharp maximum of the reaction rate for CO$_2$ contents between 2% and 5% [48], others report a constant increase of rate with increasing CO$_2$ content [49]. Therefore, it is still unclear if methanol formation proceeds via CO hydrogenation [50–54] or CO$_2$ hydrogenation [55–60]. However, most publications state that the CO$_2$ hydrogenation is intrinsically faster, as long as the right surface oxidation state is present [48, 59]. The latter is a function of the process conditions, such as CO$_2$ content, temperature, and pressure. After conventional reduction pretreatment, 30% of Cu(I) are left on the surface [41]. According to Skrzypek these Cu(I) species are involved in the rate-determining step and the key step is the hydrogenation of formate yielding methanol and a surface oxygen atom [42, 61, 62]. In this dual-site mechanism, the formate is adsorbed at the Cu(I) center, whereas Cu(0) supplies surface hydrogen. The presence of CO$_2$ in high concentrations leads to a lower activity due to an increase of surface oxygen atoms and formation of Cu(II). The presence of a CO$_2$-free syngas on the other hand was shown to lead to an overreduction of the surface and decrease of activity [48, 59]. In lower concentrations, CO leads to a decrease of surface oxygen and increasing activity [48]. These two adverse effects (overoxidation by CO$_2$ and overreduction by CO) fit well to the observations made by Klier and coworkers [48]. However, Lee and coworkers showed that this effect is additionally influenced by the gas residence time and the catalyst age. The effect described by Klier was only found at low space velocities and for fresh catalysts [59].

Under industrial process conditions, the reaction is only slightly influenced by internal mass transport [63–65]. According to Seyfert and coworkers, the effectivity factor is between 1 and 0.65 for 538–518 K at 80 bar [53]. Lommerts and coworkers showed that the rather simple Thiele modulus approach is sufficient to estimate the influence of mass transport on the overall reaction rate [66].

The methanol synthesis reaction on Cu–ZnO–Al$_2$O$_3$ is a highly complex system. Depending on the process conditions, various pathways and phenomena can occur, and a single valid mechanism is hard to find [67, 61, 68]. Therefore, the most suitable kinetic models for this reaction system incorporate all potential pathways and cover a wide range of experimental conditions, such as the Langmuir–Hinshelwood-based model [59]. Using such a model, the methanol process performance can be predicted with sufficient accuracy.

### 4.1.3. Byproducts

Commercially available Cu–ZnO–Al$_2$O$_3$ catalysts for the low-pressure synthesis of methanol permit production with high selectivity, typically above 99% referred to the added CO$_x$.

The most prominent byproducts are higher alcohols [69–71], ethers (mainly dimethyl ether, DME) [72, 73], esters (e.g., formates) [71, 72, 74], hydrocarbons [70, 75, 72], and ketones [76]. The byproduct formation can be promoted by catalyst impurities, such as alkali (higher alcohols), iron, cobalt, nickel (via typical Fischer–Tropsch reactions), or by the methanol catalyst itself (DME formation over acidic Al$_2$O$_3$).

All reactions leading to C$_2^+$ byproduct formation are controlled kinetically rather than thermodynamically [37]. The methanol purity therefore is mainly dominated by residence time [71] and temperature [75, 72]. A detailed discussion of individual byproduct classes is given in [37].

When using specially modified catalyst systems, such as alkali-doped Cu–ZnO–Al$_2$O$_3$ catalysts, the effect of byproduct formation can be used for the combined synthesis of a mixture of higher alcohols for high-octane fuel substitutes [77].

## 4.2. Catalysts

### 4.2.1. Conventional Methanol Synthesis Catalysts

The first industrial production of methanol from synthesis gas by the high-pressure process employed a catalyst system consisting of ZnO and $Cr_2O_3$. This catalyst, which was used at 25–35 MPa and 300–450 °C, was highly stable to the sulfur and chlorine compounds present in synthesis gas [78, 47, 79, 80].

Production of methanol with $ZnO–Cr_2O_3$ catalysts by the high-pressure process is no longer economical. The last methanol plant based on this process closed in the mid-1980s.

Well before the industrial realization of low-pressure methanol synthesis by ICI in the 1960s, Cu-containing catalysts were known to be substantially more active and selective than $ZnO–Cr_2O_3$ catalysts. Cu–ZnO catalysts and their use in the production of methanol were described by BASF in the early 1920s [81, 82]. These catalysts were employed at 15 MPa and 300 °C.

Their industrial use was prevented, however, by a significant sensitivity towards sulfur and halide impurities that were present in the synthesis gas available at that time.

A low-pressure catalyst for methanol synthesis was first used industrially in the process developed by ICI in 1966. This Cu–ZnO catalyst was thermally stabilized with alumina. It was used to convert extremely pure (i.e., largely free of sulfur and chlorine compounds, $H_2S$ < 0.1 ppm) synthesis gas to methanol at extremely mild conditions [83]. Under these conditions, the catalysts were highly selective and showed an excellent stability. All commercially available catalyst systems (selection shown in Table 2) are based on $Cu–ZnO–Al_2O_3$ or $Cr_2O_3$ with different additives and promoters [90, 91]. Prominent components are Zr, Cr, Mg, and rare earth metals. These promoters have a significant influence on the Cu dispersion and particle size, as well as their mobility on the catalyst surface [92].

The conventional synthesis routes for the catalysts incorporate coprecipitation of metal salt solutions using basic precipitation agents, such as sodium carbonate, ammonium carbonate, or sodium hydroxide at selected concentra-

**Table 2.** Summary of typical copper-containing catalysts for low-pressure methanol synthesis

| Manufacturer | Component | Content, atom% | Reference |
|---|---|---|---|
| IFP | Cu | 25–80 | [84] |
| | Zn | 10–50 | |
| | Al | 4–25 | |
| Süd Chemie | Cu | 65–75 | [85] |
| | Zn | 18–23 | |
| | Al | 8–12 | |
| Shell | Cu | 71 | [86] |
| | Zn | 24 | |
| | rare earth oxide | 5 | |
| ICI | Cu | 61 | [87] |
| | Zn | 30 | |
| | Al | 9 | |
| BASF | Cu | 65–75 | [88] |
| | Zn | 20–30 | |
| | Al | 5–10 | |
| Du Pont | Cu | 50 | [89] |
| | Zn | 19 | |
| | Al | 31 | |
| United Catalysts | Cu | 62 | [89] |
| | Zn | 21 | |
| | Al | 17 | |
| Haldor Topsøe | Cu | 37 | [89] |
| | Zn | 15 | |
| | Cr | 48 | |

tions, temperature, stirring speed, and pH. The obtained mixed metal salts (predominantly hydrogen carbonates) have to be further processes before they can be used for the reaction. After a drying step at approximately 120 °C, the catalyst precursor is converted to finely dispersed metal oxide by subsequent calcination at ca. 300–500 °C [83]. The calcined product is then pelleted to commercial catalyst forms. Cylindrical tablets with 4–6 mm in diameter and height are common [44, 91, 93, 94].

The catalysts have a total BET surface area of 60–100 $m^2/g$ and are activated by controlled reduction with 0.5–2% hydrogen in nitrogen at 150–250 °C, with synthesis gas, or CO [93]. Hot spots must be avoided as they lead to premature catalyst aging. In their reduced (i.e., active) form, the synthesis-active copper surfaces of commercial catalysts have a surface area of 20–30 $m^2/g$ [90].

R&D focuses on the optimization of the synthesis route for Cu–ZnO-based catalyst systems [95–97]. Especially in China, efforts are taken to develop more active and more stable catalyst systems by modifying the synthesis procedure [98–100]

### 4.2.2. Alternative Catalyst Systems

Many groups concentrate on the development of novel catalyst systems for methanol synthesis based on alternative components and formulations. The simplest alternatives are Cu–ZnO–$Al_2O_3$ based catalyst systems with various dopants (see Section 4.2.1) [101–109]. However, most modifications do not change the overall performance dramatically but rather yield slight improvements, e.g., with respect to long-term stability.

Alternative Cu-based catalyst systems can be produced by Al leaching from Cu–Al alloys yielding Raney-Cu catalysts with high surface areas [110–115]. The performance of these Raney-Cu catalysts mainly depends on the surface area, the presence of Al-residues (leading to DME formation) as well as on the leaching conditions, i.e., pH, alkali concentration, leaching time or depth, etc. [112, 113].

Other catalyst systems developed since the 1980s are based on noble metals [116]. Although already in 1928 the first catalyst for methanol synthesis based on palladium was claimed [117], new combinations containing Au or Ag [118, 119], Pd [120–124], or Pt [125] are developed. However, significantly higher catalyst costs and comparably limited improvements have prevented the use of these catalyst systems in commercial methanol production plants.

### 4.2.3. Catalyst Deactivation

The structural properties of methanol synthesis catalysts, i.e., metal surface area, dispersion, particle size, lattice defects, etc., are essential for the activity of the materials under process conditions. However, these structural properties are significantly influenced and changed by the process conditions. Especially high temperatures, presence of catalyst poisons as well as high gas flow rates have a negative influence on the catalysts resulting in a more or less pronounced reversible or irreversible decrease of activity over operation time [37, 93, 126]. Therefore, the high temperature sensitivity of the material requires controlled conditions during operation as well as during reduction. Too high hydrogen concentration during reduction or too low recycle ratio during operation can lead to high temperature peaks inside the bed or the single pellet and to accelerated sintering and degradation. The overall catalyst lifetimes are in the range of two to five years. Shorter lifetimes would significantly increase the operational costs of a methanol plant.

Besides the operational problems, which mainly lead to thermal catalyst degradation, chemical degradation can occur if catalyst poisons are present in the synthesis gas. The most prominent groups of catalyst poisons are sulfur compounds and halides:

Sulfur components, typically $H_2S$ or COS, are well known poisons for many active metals. Sulfur blocks the surface atoms of the active sites, e.g., Cu, and thus prevents further reactions [127, 128]. However, sulfur can be scavenged by ZnO, and therefore, ZnO has an additional guarding function to prevent Cu poisoning. In conventional methanol plants, sulfur is already removed, e.g., in the gas cleaning step (e.g., Rectisol gas wash) or in the water–gas shift step.

Halides do not block the catalyst surface but accelerate the sintering process and thus lead to an effective decrease of active surface [128]. When exposed to halide-containing streams, both Cu and Zn form the corresponding halides, which have significantly lower melting points than the respective metals or metal oxides ( 426 °C vs. 1085 °C for CuCl and Cu(0), respectively, and 318 °C vs. 1975 °C for $ZnCl_2$ and ZnO, respectively).

In addition to sulfur and halides, several other impurities, such as arsine [129], phosphines [130], iron carbonyl, and nickel carbonyl [128, 131] have been discussed. These carbonyl components can be present when operating at high CO partial pressures and low temperatures with unsuitable base materials. Carbonyls lead to a decrease of selectivity due to deposition of iron and nickel and promotion of Fischer–Tropsch side reactions. In addition, these metals can interact with the active metal surface and lead to an activity decrease by formation of inactive alloys. A detailed overview over catalyst poisons in liquid phase methanol synthesis (LPMEOH) is given in [130].

To date, only few attempts can be found to predict catalyst deactivation quantitatively under industrial conditions [132, 133].

# 5. Process Technology

The oldest process for the industrial methanol production is the dry distillation of wood, but this no longer has practical importance. Other processes, such as the oxidation of hydrocarbons, production as a byproduct of the Fischer–Tropsch synthesis according to the Synthol process, high-pressure (HP) methanol process (25–30 MPa), and medium-pressure (MP) methanol process (10–25 MPa) are not important anymore.

Methanol is currently produced on an industrial scale exclusively by catalytic conversion of synthesis gas according to the principles of the low-pressure (LP) methanol process (5–10 MPa).

The main advantages of the low-pressure processes are lower investment and production costs, improved operational reliability, and greater flexibility in the choice of plant size.

Industrial methanol production can be subdivided into three main steps:

1. Production of synthesis gas
2. Synthesis of methanol
3. Processing of crude methanol

## 5.1. Production of Synthesis Gas

All carbonaceous materials, such as coal, coke, natural gas, petroleum, and fractions obtained from petroleum (asphalt, gasoline, gaseous compounds) can be used as starting materials for synthesis gas production. Economy is of primary importance with regard to the choice of raw materials. Long-term availability, energy consumption, and environmental aspects must also be considered.

Natural gas is generally used in the large-scale production of synthesis gas for methanol synthesis. The composition of the synthesis gas required for methanol synthesis is characterized by the stoichiometry number $S$:

$$S = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$$

where the concentrations of relevant components are expressed in volume percent. The stoichiometry number should be at least 2.0 for the synthesis gas mixture. Values above 2.0

indicate an excess of hydrogen, whereas values below 2.0 mean a hydrogen deficiency relative to the stoichiometry of the methanol formation reaction. Deficiency in hydrogen will reduce the selectivity to methanol drastically, whereas an excess of hydrogen increases the size of the synthesis loop because the hydrogen is accumulated there. Therefore, a synthesis gas composition with a stoichiometric number slightly above 2.0 is the optimum for methanol synthesis.

### 5.1.1. Natural Gas

Most methanol produced worldwide is derived from natural gas. Natural gas can be cracked by steam reforming, autothermal reforming, a combination thereof, and by partial oxidation (Fig. 3, see also → Gas Production, 1. Introduction).

In steam reforming the feedstock is catalytically cracked in the absence of oxygen with the addition of steam and possibly carbon dioxide (→ Gas Production, 2. Processes, Chap. 1). Conventional steam reforming results in a stoichiometric number of the synthesis gas produced well above 2.0, i.e., ∼2.8. By the addition of $CO_2$ either up or downstream of the steam reformer, the stoichiometric number can be adjusted to the desired value of slightly above 2.0. The reaction heat required is supplied externally.

In autothermal reforming, the conversion of the feedstock is achieved by partial oxidation with oxygen and reaction on a Ni-based catalyst. The heat for reaction is provided by the exothermic partial oxidation reaction. The synthesis gas obtained is characterized by a deficiency in hydrogen, i.e., hydrogen has to be added to the synthesis gas before routing to the methanol synthesis loop.

In a combination of the two processes, only part of the natural gas stream is subjected to steam reforming [134] see also → Gas Production, 2. Processes, Section 1.5. The remainder is fed together with the steam reformed gas to an autothermal reformer (ATR) filled with Ni-based catalyst. In the ATR, the natural gas is partially oxidized by oxygen. The stoichiometric number of the synthesis gas can be adjusted to slightly above 2.0, by adjusting the split
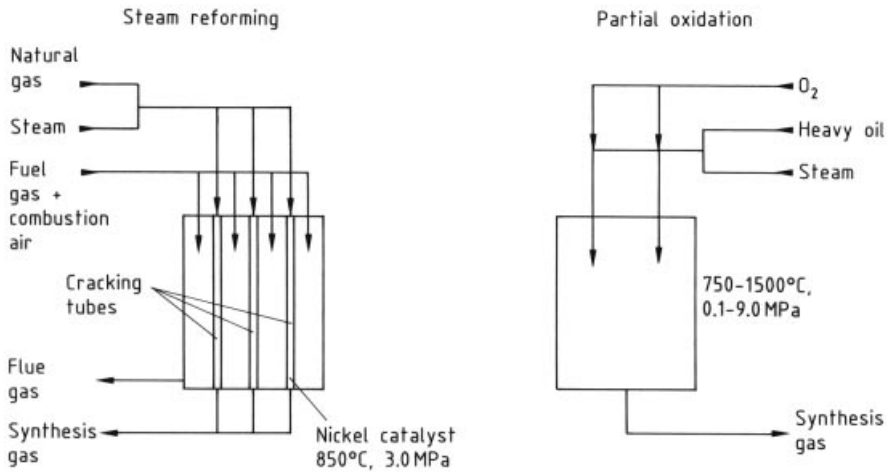
Steam reforming

Partial oxidation



**Figure 3.** Processes for producing synthesis gases

between steam and autothermal reforming and selecting the proper process parameters.

In partial oxidation, cracking takes place without a catalyst ($\rightarrow$ Gas Production, 2. Processes, Chap. 2). Reaction heat is generated by direct oxidation of part of the feedstock with oxygen.

### 5.1.2. Other Raw Materials

Higher hydrocarbons (e.g., liquefied petroleum gas, refinery off-gases, and particularly naphtha) are also used as raw materials for synthesis gas used in methanol production plants ($\rightarrow$ Gas Production, 2. Processes, Section 1.1.). They are processed mainly by steam reforming. Crude oil, heavy oil, tar, and asphalt products ($\rightarrow$ Gas Production, 2. Processes, Section 2.1.) can also be converted into synthesis gas, but this is more difficult than with natural gas. Their sulfur content is considerably higher (0.7–1.5% $H_2S$ and COS) and must be decreased. The produced synthesis gas also contains excess carbon monoxide and must, therefore, be subjected to shift conversion with water. The resulting excess of carbon dioxide is removed from the gas. Gas cleaning and carbon dioxide removal can be achieved e.g., within a Rectisol process.

Coal can be converted into synthesis gas with steam and oxygen by a variety of processes at different pressures (0.5–8 MPa)

and temperature (400–1500°C); see also $\rightarrow$ Coal, Section 9.4.; $\rightarrow$ Gas Production, 2. Processes, Chap. 3. The coal-based synthesis gas must be desulfurized and subjected to shift conversion to obtain the required stoichiometry.

### 5.2. Synthesis

Important reactions (Eqs. 1–3) for the formation of methanol from synthesis gas are discussed in Section 4.1. In one pass a carbon conversion of only 50% to 80% can be achieved, depending on the synthesis gas composition and the selected process. Therefore, after methanol and water are condensed and removed, the remaining gas must be recycled to the reactor. A simplified flow diagram for LP methanol syntheses is shown in Figure 4. The make-up synthesis gas is brought to the desired pressure (5–10 MPa) in a compressor (f). The synthesis gas (make-up gas; MUG) is mixed with the unreacted recycle gas and routed to a heat exchanger (b) in which energy from the hot gas leaving the reactor is transferred to the gas entering the reactor. The exothermic formation of methanol takes place in the reactor (a) at 200–300 °C. The heat of reaction can be dissipated in one or more stages. The gas mixture leaving the reactor is cooled further (c) after passing through the heat exchanger (b); the heat of condensation of methanol and water can be utilized at another point in the process.
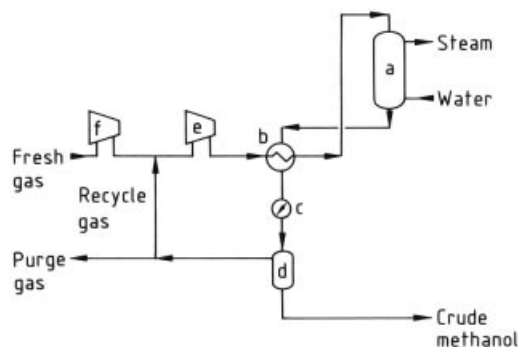
**Figure 4.** Methanol synthesis
a) Reactor; b) Heat exchanger; c) Cooler; d) Separator;
e) Recycle compressor; f) Fresh gas compressor

Crude methanol is separated from the gas phase in a separator (d) and flashed before being distilled. Gas from the separator is recycled to the suction side of the recycle compressor (e). The quantity of the purge gas from the loop is governed by the concentration of inert substances and the stoichiometric number. If hydrogen is needed to adjust the composition of the fresh gas to give the required stoichiometry number, it can be recovered from the purge gas by various methods (e.g., pressure swing absorption, membrane separation). The purge gas is normally used for reformer heating.

Until 1997, the industrial LP methanol processes differed primarily in reactor design. The maximum capacity of methanol plants was 2 500 to 3 000 t/d. Later, more efforts were taken to combine a beneficial reactor technology with suitable methods to produce large amounts of clean synthesis gas that was needed for large-scale plants.

In 1997, Lurgi presented their MegaMethanol process [135], where a combination of different reactor types together with an adopted gas production (see also → Gas Production, 5. Examples of Complex Gas Production Plants, Chap. 1) paved the way to capacities up to 10 000 t/d single train capacity. Different concepts have been developed by technology companies using not only a single loop with one type of reactor but a variety of different combinations to ideally suit the needs of site and customer. In 2011, the major part of the operating plants was licensed by Lurgi (27%), JM/Davy (25%),

Topsøe (16%) followed by MGC, JM/Uhde, JM/Jacobs, JM/Others, JM/Toyo [136]. All technologies are based on highly integrated technology concepts including all steps from gasification and gas cleaning to synthesis and workup. Thus, high energy and carbon efficiencies up to 67% and 83%, respectively, can be reached (calculated from [137]).

### 5.2.1. Reactor Design

Methanol is produced on industrial scale since the 1960s and still several different basic design are available and used. Depending on the given prerequisites (e.g., carbon source, availability of utilities, heat integration in 'Verbund sites', etc.), different reactor and operation concepts may be chosen. Among those are adiabatic or quasi-isothermal, water or gas-cooled, radial, axial, and axial-radial reactors. These reactor types enable the tailoring of mass and heat transfer inside the catalyst bed and thus allow an optimization of the methanol formation in terms of kinetics, thermodynamics, selectivity, and catalyst lifetime. In all cases, a compromise between sufficient reaction rate and sufficient heat removal must be found.

A summary of current methanol reactor developments is given in [138].

*Adiabatic Reactors.* In adiabatic reactors with a single catalyst bed, the reaction is quenched by adding cold gas at several points. Thus, the temperature profile along the axis of the reactor has a sawtooth shape.

In reactors where synthesis gas flows through several reactor beds arranged axially in series the heat of reaction is removed by intermediate coolers. In these reactors, the synthesis gas flows axial, radial, or axial/radial through the catalyst beds [139–141].

*Quasi-Isothermal Reactors.* The standard quasi-isothermal reactor employs a tubular reactor with cooling by boiling water [142]. The catalyst is located in tubes that are surrounded by boiling water for heat of reaction removal. The temperature of the cooling medium is adjusted by a preset pressure in the steam drum. Synthesis gas flows axially through the tubes.

The Variobar reactor [143] consists of a shell-and-tube reactor coiled in several tiers, whose cooling tubes are embedded in the catalyst packing. The reactor temperature is adjusted by water-cooling. As in standard quasi-isothermal reactors, the heat of reaction is utilized to produce steam, which can be used, for example, to drive a turbine for the compressor or as an energy source for subsequent methanol distillation.

In quasi-isothermal reactors with catalyst on the shell side, the synthesis gas flows either axially, radially, or axially-radially through the catalyst bed. The heat of reaction can not only be transferred to boiling water but also to reaction gas. This reactor type is called gas-cooled reactor.

In the so-called superconverter, double-walled tubes are filled in the annular space with catalyst [144]. The synthesis gas first flows through the inner tube to heat it up and then, in the reverse direction, through the catalyst between the two tubes releasing heat of reaction and transferring it to the cold feed gas. The outer tubes are cooled by water.

## 5.2.2. Large-Scale Methanol Synthesis Loop Designs

Especially in remote areas, methanol is discussed as a well transportable liquid energy carrier, e.g., instead of natural gas. To be economical, scale is essential for those projects. In order not to exceed equipment, piping, and valve dimensions the amount of gas flowing through the loop has to be minimized, i.e., the conversion per pass has to be increased. Consequently, the gas entering the catalyst bed is quite reactive, because the dilution with nonreacted recycled synthesis gas is rather low.

One design example is the Lurgi Combined Converter Methanol Synthesis (Fig. 5), which is part of the MegaMethanol process.

The reaction is split into two conversion steps. As in the LP methanol syntheses, the gas is compressed to the selected pressure (5 to 10 MPa) by a synthesis gas compressor and preheated to the inlet temperature needed for the first methanol converter. This reactor is a quasi-isothermal boiling water reactor with catalyst in
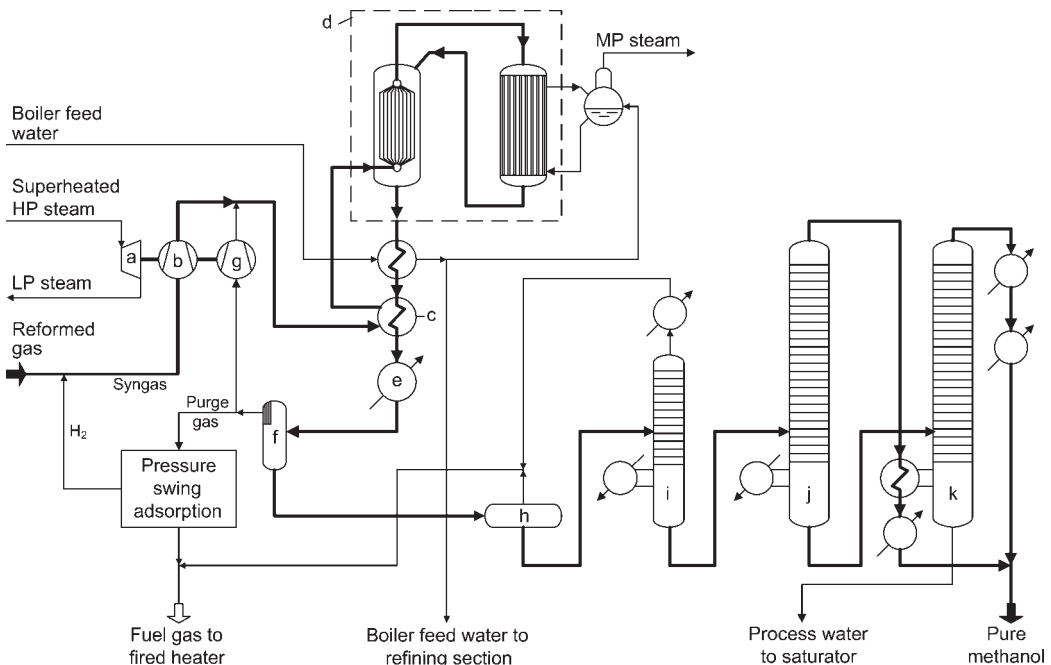


**Figure 5.** Process scheme for the Lurgi MegaMethanol synthesis process
a) Turbine for synthesis gas and recycle compressor; b) Synthesis gas compressor; c) Trim heater; d) Combined converter system; e) Final cooler; f) Methanol separator; g) Recycle gas compressor; h) Expansion vessel; i) Light ends column; j) Pure methanol pressure column; k) Atmospheric methanol column

the tubes to ensure the most efficient heat removal because the reaction gas entering this reactor is very reactive and overheating of the catalyst has to be avoided. In a second converter, the preconverted gas is routed to the shell side of the gas-cooled methanol reactor, which is filled with catalyst at the shell side. The final conversion to methanol is achieved at continuously reduced operating temperatures along the reaction route. The decreasing reaction temperature provides a permanent driving force for conversion to methanol. The heat of reaction is used to preheat the reactor inlet gas inside the tubes of the first methanol converter. The reactor outlet gas is cooled; crude methanol is separated and routed for purification to the distillation section. Unreacted gas is compressed and recycled. Part of the unreacted gas is purged out of the loop to avoid accumulation of inerts.

A second example is the series loop technology of Davy Process Technology for exothermic synthesis gas compositions (Fig. 6) [145]. The loop design is also based on the principles of the LP methanol synthesis. Instead of arranging two reactors in parallel, the reactors are arranged in series where the same circulation gas is used twice, first in the HP-reactor and secondly in the LP-reactor. The driving force for the reaction is maintained by condensing methanol between the two reactors [136].

## 5.3. Alternative Synthesis Routes

### 5.3.1. $CO_2$-to-Methanol

Since the early 1990s, the chemical valorization of $CO_2$ by hydrogenation to methanol has been in the focus of research. However, after the general feasibility and first concepts for catalysts and processes were shown [146–148], this approach was not of commercial interest. Due to increasing awareness of the necessity to reduce $CO_2$ emissions for environmental reasons as well as due to government politics (e.g., $CO_2$ tax and cap-and-trade programs) [149], this topic again gains more industrial relevance [150]. Several companies have realized that $CO_2$ emission reduction and the development of $CO_2$ utilizing technologies may be an essential step towards a more sustainable industrial world [151–155].

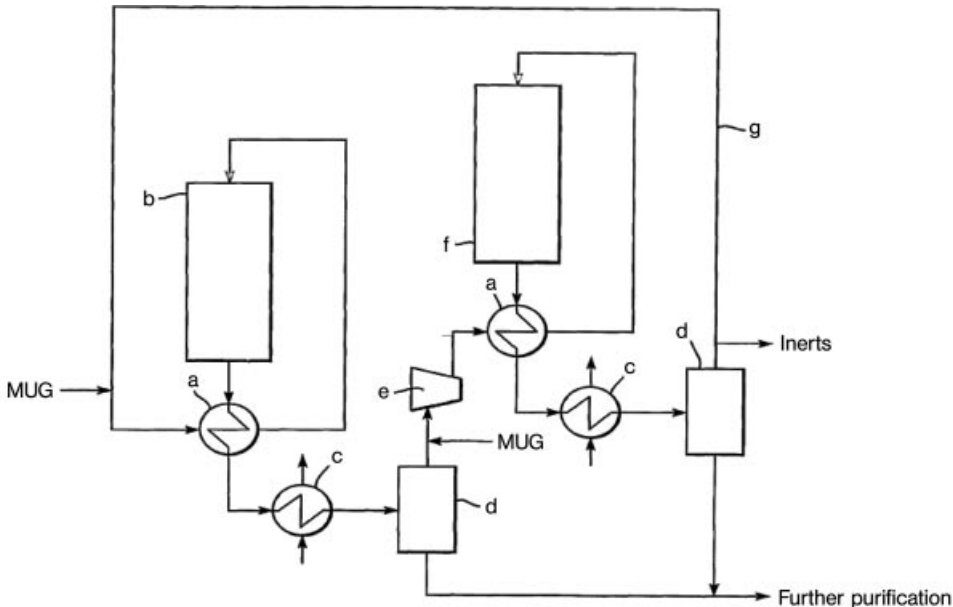Since the 1990s, much effort has been spent on the focused development of catalyst



**Figure 6.** Process scheme for the Davy series loop methanol process
a) Interchanger; b) Reactor; c) Condenser; d) Gas–liquid separator; e) Circulator; f) Final reactor; g) Recycle gas line

systems for the hydrogenation of $CO_2$ to methanol [154, 146, 147]. This work is still ongoing [121, 155, 156]. Several companies claim specialized process concepts based on simple and conventional technologies [148, 157] or more indirect pathways, such as CAMERE (i.e., $CO_2$-to-methanol via the reverse water–gas shift process) [158]. Although the economic relevance has been pointed out several times, pilot-scale results are scarce [148, 154, 159]. The only pilot or demonstration-scale projects are by Mitsui Chemicals [151] and Carbonrecycling, Iceland. In the latter case, geothermal $CO_2$ and heat are used to produce methanol via water electrolysis and $CO_2$ hydrogenation [160].

The basic knowledge about the $CO_2$-to-methanol technology is already available. Although the catalyst systems may still be improved, the real challenge of this technology is the production of renewable hydrogen from various energy sources as well as the economically feasible production of clean $CO_2$ from waste gas streams. It is the political and ecological (and later perhaps also economical) drivers that decide if and when this technology comes to market.

### 5.3.2. Liquid Phase Methanol Synthesis (LPMEOH)

An alternative method to produce methanol is to convert CO with hydrogen in a liquid phase, in most cases methanol. When using suitable reaction conditions and catalyst systems containing alkali components, significant productivities of up to 1.3 kg $kg_{cat}^{-1}$ $h^{-1}$ can be reached [161]. During the reaction in the liquid phase, a different mechanism occurs including methanol (or higher alcohol) carbonylation to the respective methyl ester followed by hydrogenolysis to the respective alcohol and methanol [162]. In the late 1990s, a demonstration-scale project plant was put in operation (DOE together with Eastman and Air Products). However, it was found that the catalyst lifetimes are inferior to conventional processes (best case: 0.17%/d at 215 °C). Both water and $CO_2$ show a negative effect on the catalyst performance [163]. However, this concept is further developed [164–167].

### 5.3.3. Direct Oxidation of Methane

The selective direct oxidation of methane to methanol is one of the 'dream reactions'. The reaction sounds simple, but from the kinetic as well as from the thermodynamic point of view this reaction is highly unfavorable. Up to now, most catalyst systems, such as Fe [168–170], Mo [171], or Rh [172] yield either low conversion ($<$ 10%) and/or low selectivities ($<$ 80%) [167–170]. Although some companies claim simple efficient processes for the synthesis of methanol mainly for small gas sources [173], this technology has not yet been commercialized. However, more alternative catalyst systems, e.g., heterogeneous Pt-CTF (covalent triazine-based framework) catalysts in a sulfuric acid medium, are developed [174] and may be more promising.

### 5.4. Distillation of Crude Methanol

Crude methanol leaving the reactor contains water and other impurities (see Section 4.1). The amount and composition of these impurities depend on reaction conditions, feed gas, and type and lifetime of the catalyst. Crude methanol is made slightly alkaline by the addition of small amounts of aqueous caustic soda to neutralize lower carboxylic acids and partially hydrolyze esters.

The crude methanol contains low-boiling and high-boiling components (light and heavy ends). The light ends include mainly dissolved gases (e.g., $CO_2$), dimethyl ether, methyl formate, and acetone. The heavy ends include higher alcohols, long-chain hydrocarbons, higher ketones, and esters of lower alcohols with formic, acetic, and propionic acids. Higher waxy hydrocarbons consisting of a mixture of mostly straight-chain $> C_8$ compounds are also formed in small amounts. They have low volatility and thus remain in the distillation bottoms, from which they can easily be removed because of their low solubility in water and low density.

The impurities in crude methanol are generally separated in two stages. First, all components boiling at a lower temperature than methanol are removed in a light ends column. Pure methanol is then distilled overhead in one or more distillation columns (Fig. 5, Fig. 6). If the

columns operate at different pressures, the heat of condensation of the vapors of the column operating at higher pressure can be used to heat the column at lower pressure.

In case the process water contains slight impurities, i.e., the bottom product of the heavy ends column, either a side draw-off or an additional column for purification is required.

Some components form azeotropic mixtures with methanol [175], such as acetone, ethyl formate, methyl acetate, ethyl acetate, and methyl proprionate.

## 5.5. Construction Materials

Carbon steel or low-molybdenum steels are normally used as construction materials in methanol synthesis. Because organic acids are likely to be encountered in the methanol condensation stage, stainless steels are generally used then. Damage due to acids can also be prevented in the distillation section by the addition of small amounts of dilute caustic soda.

Stainless steels are normally employed in equipment operating at conditions in which the formation of iron pentacarbonyl is likely. This applies, for example, to heat exchangers. Contamination with iron pentacarbonyl should be avoided because it decomposes at the temperatures used for methanol synthesis. Iron deposited on the catalyst poisons it and promotes the formation of higher hydrocarbons (waxy products).

# 6. Handling, Storage, and Transportation

## 6.1. Explosion and Fire Control

The flammability of methanol and its vapors represents a potential safety problem. The flash point is 12.2°C (closed cup) and the ignition temperature 470°C; in Germany methanol is thus included in ignition group B of the VbF [176].

Methanol vapor is flammable at concentrations of 5.5–44 vol%. The saturated vapor pressure at 20°C is 128 kPa; a saturated methanol–air mixture is thus flammable over a wide temperature range. Methanol is included in ignition group G1, explosion class 1 (ExRL).

In premises and workshops in which the presence of methanol vapor is likely, electrical equipment must be designed in accordance with the relevant regulations:

- Guidelines for explosion protection (ExRL)
- Regulations governing electrical equipment in explosion hazard areas (ElE×V)
- DIN VDE 0165
- DIN EN 50 014–50 020

For international guidelines on the handling of methanol, publications of the Manufacturing Chemists' Association should be consulted [177].

Pure, anhydrous methanol has a very low electrical conductivity. Measures to prevent electrostatic charging must therefore be adopted when transferring and handling methanol.

*Fire Prevention.* The VbF restrictions on the amount of methanol that can be stored in laboratory premises should be observed. When large amounts of methanol are stored in enclosed spaces, monitoring by means of lower explosion limit monitors is desirable.

Permanently installed fire-extinguishing equipment should be provided in large storage facilities. Water cannons are generally installed in storage tank farms to cool steel constructions and neighboring tanks in the event of fire. Large tanks should have permanently installed piping systems for alcohol-resistant fire-extinguishing foams.

*Fire Fighting.* Conventional fire-extinguishing agents, such as powder, carbon dioxide, or Halon can be used for small fires. Water is unsuitable as an extinguishing agent for fires involving large amounts of methanol because it is miscible with the compound; mixtures containing small amounts of methanol may also burn. Protein-based alcohol-resistant foams are suitable.

A methanol flame is practically invisible in daylight, which complicates fire fighting. The methanol flame does not produce soot, although formaldehyde and carbon monoxide form during combustion when oxygen is lacking.

Respirators must therefore be worn when fighting fires in enclosed areas.

## 6.2. Storage and Transportation

*Small-Scale Storage.* Small amounts ($\leq$ 10 L) of methanol for laboratory and industrial use are stored in glass bottles or sheet-metal cans; amounts up to 200 L are stored and transported in steel drums. Some plastic bottles and containers cannot be used because of their permeability and the danger of dissolution of plasticizers. High-density polyethylene and polypropylene are suitable, whereas poly(vinyl chloride) and polyamides are unsuitable.

*Large-Scale Storage.* Large amounts of methanol are stored in tanks that correspond in design and construction to those used for petroleum products; cylindrical tanks with capacities from a few hundred cubic meters to more than 100 000 m$^3$ are normally used. With fixed-roof tanks, special measures (e.g., nitrogen blanketing) should be adopted to prevent the formation of an ignitable atmosphere in the space above the liquid surface. Emission of methanol may occur if the level fluctuates. To avoid these problems, large tanks are often equipped with a scrubber system or floating roofs; attention should therefore be paid to guard against entry of rainwater.

For anhydrous and carbon dioxide-free methanol tanks, pipelines and pumps can be constructed from normal-grade steel; seals can be made from mineral fiber, graphite, and metal. Styrene–butadiene rubber, chlorine–butadiene rubber, and butyl–chlorobutyl rubber can be used for shaft seals.

*Large-Scale Transportation.* Methanol is traded worldwide. The recent trend toward relocating production to sites that are remote from industrial centers where inexpensive natural gas is available means that ca. 30% of the methanol produced worldwide must be transported by sea to consumer countries (Japan, Europe, United States). Specially built tankers with capacities up to 40 000 t are available for this purpose. In Asia the tendency goes towards 50 000 to 70 000 t tanker capacities. Ships built to transport petroleum products are also used. However, most of the methanol is transported by dedicated vessels.

The most important European transshipment point for methanol is Rotterdam. Methanol is distributed to inland industrial regions mainly by inland waterways on vessels with capacities up to 1 000 to 2 000 t. Due to transportation with nondedicated vessels impurities can be introduced into the methanol due to frequent change of cargo. Analysis prior to delivery is generally essential.

Methanol is also transported by road and rail tank cars. Permanently coupled trains consisting of several large tank cars with common filling, discharge, and ventilation lines are used to supply large customers.

Transportation via pipeline is only of importance for supplying individual users within enclosed, self-contained chemical complexes.

*Safety Regulations Governing Transportation.* The transportation of methanol as less-than-carload freight in appropriate vessels, containers, and bulk, is governed by specific regulations that differ from country to country. An effort is being made, and is already well advanced, to coordinate these regulations within the EC. Relevant legal regulations governing less-than-carload and bulk transportation by sea, on inland waterways, and by rail, road, and air are as follows [178]:

| | |
|---|---|
| IMDG Code (D-GGVSee) | D 3328/E-F 3087, Class 3.2, UN No. 1230 |
| RID (D-GGVE) | Class 3, Rn 301, Item 5 |
| ADR (D-GGVS) | Class 3, Rn 2301, Item 5 |
| ADNR | Class 3, Rn 6301, Item 5, Category Kx |
| European Yellow Book | No. 603–001–00-X |
| EC Guideline/D VgAst | No. 603–001–00-X |
| Germany (Land, VbF) | B |
| Great Britain | Blue Book: Flammable liquid and IMDG Code E 3087 |
| United States | CRF 49, Paragraph 172.1.1, flammable liquid |
| IATA | RAR, Art. No. 1121/43, flammable liquid |

## 7. Quality Specifications and Analysis

*Methanol for Laboratory Use.* Methanol is available commercially in various purity grades for fine chemicals:

*"Purum" quality (>99.0%).* This quality corresponds to commercial grade AA methanol. Methanol with this specification typically has a purity of ≥ 99.85%.

*"Puriss. p.a." quality (>99.8%).* This methanol has a certified analytical quality with specifications in terms of water content and evaporation residues.

*Highest purity, e.g., CHROMASOLV Methanol (≥ 99.9%).* This methanol is extremely pure and can be used for spectroscopic or semiconductor applications. Specifications exist mainly concerning spectroscopic properties, like UV–VIS absorbance, IR, or fluorescence activity as well as chemical impurities, such as carbonyls and residual acids and bases.

***Commercial Methanol.*** In addition to laboratory grades, commercial methanol is generally classified according to ASTM purity grades A, AA, and IMPCA specification (Table 3). The Methanol Institute provides the current version of the specification [179]. In China and Russia, slightly different specifications are applied. However, methanol for chemical use normally corresponds to Grade AA.

In addition to water, typical impurities include acetone and ethanol. When methanol is delivered by ships or tankers used to transport other substances, contamination by the previous cargo must be expected.

Comparative ultraviolet spectroscopy has proved a convenient, quick test method for deciding whether a batch can be accepted and loaded. Traces of all chemicals derived from aromatic parent substances, as well as a large number of other compounds, can be detected.

Further tests for establishing the quality of methanol include measurements of boiling point range, density, permanganate number, turbidity, color index, and acid number. Tests that are more comprehensive include water determination according to the Karl Fischer method and gas chromatographic determination of byproducts. However, the latter is relatively expensive and time consuming because several injections using different columns and detectors must be made due to the variety of byproducts present.

The most important standardized test methods for methanol are:

| | |
|---|---|
| ASTM D 891 | specific gravity |
| ASTM D 1078 | distillation range |
| ASTM D 1209 | color index |
| ASTM D 1353 | dry residue |
| ASTM D 1363 | permanganate number |
| ASTM D 1364 | water content |
| ASTM E 346 | carbonylic compound |
| ASTM D 1613 | acid content |

Methanol obtained directly from synthesis without any purification, or with only partial

**Table 3.** Federal specifications for pure methanol in the United States O-M-232L and IMPCA

| Property | Grade A | Grade AA | IMPCA |
|---|---|---|---|
| Ethanol content, mg/kg | | < 10 | < 50 |
| Acetone content, mg/kg | < 30 | < 20 | < 30 |
| | | | < 30 |
| | | | < 5 |
| Acid content (as acetic acid), mg/kg | < 30 | < 30 | < 30 |
| Color (PtCo) | < 5 | < 5 | < 5 |
| Carbonizable impurities, color (PtCo) | < 30 | < 30 | < 30 |
| Distillation range (101.3 kPa), °C must include 64.6±0.1°C | < 1 | < 1 | < 1 |
| Nonvolatile matter, mg/100 mL | < 10 | < 10 | < 0.8 |
| Specific gravity (20/20°C), kg/L | 0.7928 | 0.7928 | 0.791–0.793 |
| Permanganate time, min | > 30 | > 30 | > 60 |
| Methanol content, wt% | > 99.85 | > 99.85 | > 99.85 |
| Water content, wt% | < 0.15 | < 0.10 | < 0.10 |
| Odor | characteristic, nonresidual | characteristic, nonresidual | |
| Appearance | free of opalescence, suspended matter and sediment | free of opalescence, suspended matter and sediment | clear and free of suspended matter |
| Chloride as Cl⁻, mg/kg | | | 0.5 |
| Sulfur, mg/kg | | | 0.5 |
| Total iron, mg/kg | | | 0.1 |
| Hydrocarbons | | | pass test |

purification, is sometimes used. This crude methanol can be used for energy generation (fuel methanol), for the manufacture of synthetic fuels, and for specific chemical and technical purposes, such as dimethyl ether or olefin production (MTO grade methanol) [180]. It is normally not commercially available. Composition varies according to synthesis conditions. Principal impurities include 5–20 vol% water, higher alcohols, methyl formate, and higher esters. The presence of water and esters can cause corrosion during storage due to the formation of organic acids (see Section 6.2); remedies include alkaline adjustment with sodium hydroxide and, if necessary, the use of corrosion-resistant materials.

# 8. Environmental Protection

Methanol is readily biodegraded. Most microorganisms possess the enzyme alcohol dehydrogenase, which is necessary for methanol oxidation. Therefore, there is no danger of its accumulation in the atmosphere, water, or ground. The biological stages of sewage treatment plants break down methanol almost completely. In Germany methanol has been classified as a weakly hazardous compound in water hazard Class 1 (WGK I, § 19 Wasserhaushaltsgesetz). In case of accidents during transport, large amounts of methanol must be prevented from penetrating into the groundwater or surface waters to avoid contaminating drinking water. Little is known about the behavior of methanol in the atmosphere. Emissions occurring during industrial use are so small that harmful influences can be ignored. That situation could alter, however, if methanol were used on a large scale as an alternative to petroleum-based fuels.

In methanol production, residues that present serious environmental problems are not generally formed. All byproducts are used when possible; for example, the condensate can be processed into boiler feedwater, and residual gases or low-boiling byproducts can be used for energy production. The only regularly occurring waste product that presents some difficulties is the bottoms residue obtained after distillation of pure methanol; it contains water, methanol, ethanol, higher alcohols, other oxygen-containing organic compounds, and variable amounts of paraffins. The water-soluble organic substances readily undergo biological degradation. The insoluble substances can be incinerated safely in a normal waste incineration unit. In some cases, this residual water is also subjected to further distillative purification. The resultant mixture of alcohols, esters, ketones, and aliphatics can be added in small amounts to carburetor fuel.

The spent catalysts contain auxiliary agents and supports as well as copper (synthesis), nickel (gas generation), and cobalt and molybdenum (desulfurization) as active components. These metals are generally recovered or otherwise utilized.

Modern steam reformers can be fired so that emission of nitrogen oxides ($NO_x$) in the flue gas is maintained below 200 mg/m$^3$ without having to use secondary measures.

# 9. Uses

## 9.1. Use as Feedstock for Chemical Syntheses

Approximately 70% of the methanol produced worldwide is used in chemical syntheses [181]. In order of importance: Formaldehyde, methyl *tert*-butyl ether (MTBE), acetic acid, dimethyl ether (DME), propene, methyl methacrylate and dimethyl terephthalate (DMT). The use for energy and fuel applications, either directly or in form of methanol downstream products, is gaining more importance, especially in today's emerging economies.

*Formaldehyde* is the most important product synthesized from methanol (→ Formaldehyde, Chap. 4.); in 2011, 28% of the methanol produced worldwide was used to synthesize this product. Although an annual estimated increase in formaldehyde production could be observed during the last years, the relative share concerning methanol consumption decreased because the other products (especially propene and fuel applications) increased more considerably.

The processes employed are all based on the oxidation of methanol with atmospheric oxygen. They differ mainly with regard to temperature and nature of the catalyst used.

**Methyl tert-Butyl Ether** (MTBE) is produced by reacting methanol with isobutene on acid ion exchangers (→ Methyl *tert*-Butyl Ether). This ether is an ideal octane booster and became important due to the introduction of unleaded grades of gasoline and awareness of the possible harmfulness of aromatic high-octane components during the last decades. However, due to safety issues (e.g., MTBE release from storage tanks due to the high vapor pressure), this product was not well accepted during the last years, especially in the western countries. This led to a decrease in methanol consumption from 27% in 1996 to only 11% in 2011. Today, the commercial interest has shifted to ethyl *tert*-butyl ether (ETBE) as a MTBE substitute. Nevertheless, the overall MTBE production is likely to rise again due to the increasing usage and production capacities in the emerging economies, such as Asia and Middle East [182].

**Acetic Acid.** 11% of the methanol produced is used to synthesize acetic acid, and annual growth rates of 4% until 2013 are estimated [183]. Acetic acid is produced by carbonylation of methanol with carbon monoxide in the liquid phase with cobalt–iodine, rhodium–iodine, or nickel–iodine homogeneous catalysts (→ Acetic Acid, Section 4.1.). The older BASF process operates at 65 MPa, whereas more modern processes (e.g., the Monsanto process) operate at 5 MPa. By varying operating conditions, the synthesis can also be modified to produce acetic anhydride or methyl acetate.

**Methanol to X: Gasoline, Olefins, Propene, Aromatics.** In the intensive search after the oil crisis for routes to alternative fuels, processes were developed that allowed fuels to be produced from synthesis gas with methanol as an intermediate. Mobil in the United States has contributed decisively to the development of such processes, which involve mainly the reaction of methanol on zeolite catalysts. The most important is methanol-to-gasoline (MTG) synthesis.

The New Zealand government and Mobil built and operate a plant that produces 4 500 t/d of methanol from natural gas, and converts it into 1 700 t/d gasoline.

Further synthesis routes that become more important are the methanol-to-olefins (MTO) and methanol-to-propene (MTP) as well as methanol-to-aromatic compounds (MTA) processes [184]. The first two technologies have been successfully demonstrated during the last years. The first DMTO (DICP methanol-to-olefins, Shenhua Baotou) and MTP (Lurgi) plants have been commissioned in 2010/2011 and consumed $3 \times 10^6$ t methanol in 2011. Especially in China, this alternative synthesis route has gained significant industrial relevance because it allows the production of propene–polypropylene based on coal as sole carbon source (→ Coal Liquefaction). Expected capacities for MTO/MTP were 1.1 and $5.1 \times 10^6$ t/a of olefins (C2 and C3) for 2010 and 2011–2015, respectively [185].

**Dimethyl Ether and Others.** A product that received great attention as a result of the discussion of environmental damage caused by chlorofluorocarbons is dimethyl ether (→ Dimethyl Ether). It can be used as an alternative propellant for sprays. Compared to propane–butane mixtures also used as propellants, its most important feature is its higher polarity and, thus, its better solubilizing power for the products used in sprays. DME is also used as a solvent, organic intermediate, and in adhesives. The overall share of methanol consumption was approximately 7% [181]. When coupled to conventional large-scale methanol plants, the DME production process can profit from the operating efficiency of the scale leading to DME production capacities of more than 3 000 t/d [159].

Methanol is used to synthesize a large number of other organic compounds:

| | |
|---|---|
| Formic acid | preservatives, pickling agents |
| Methyl esters of organic acids | solvents, monomers |
| Methyl esters of inorganic acids | methylation reagents, explosives, insecticides |
| Methylamines | pharmaceutical precursors, auxiliaries, absorption liquids for gas washing and scrubbing |
| Trimethylphosphine | pharmaceuticals, vitamins, fragrances, fine chemicals |
| Sodium methoxide | organic intermediates, catalyst |
| Methyl halides | organic intermediates, solvents, propellants |
| Ethylene | organic intermediates, polymers, auxiliaries (→ Ethylene) |

## 9.2. Use as Energy Source

Methanol is a promising substitute for petroleum products if they become too expensive for use as fuels. As a result of the oil crisis in the early 1970s, a number of projects were started based on the assumption that the use of methanol produced from coal would be more economical in the medium term than the use of petroleum products. The estimates made at the beginning of the 1980s proved to be too optimistic, however, with regard to costs and to overcoming technical or environmental problems involved in producing synthesis gas from coal, and too pessimistic with regard to the price and availability of crude oil. Nearly all the large-scale projects for coal utilization have been discontinued at that time. Today, the situation has changed again. Especially in emerging economies like China and India, coal is gaining importance as feedstock for energy and chemical products, especially if no natural gas is available ($\rightarrow$ Coal Liquefaction). It is widely accepted that coal will become a more important feedstock during the next decades [186]. When talking about chemical coal use, the most promising and already technologically proven routes go via Fischer–Tropsch or methanol synthesis. Methanol itself as well as several downstream products, such as MTBE, DME, or MTG-gasoline can be used for energy and fuel applications. Some authors propagate this approach and introduced the 'methanol economy' based on methanol from coal, residues, biogas, $CO_2$, or other carbon sources and covering the complete range of products needed for future transportation and energy applications [187].

***Methanol as a Fuel for Otto Engines.*** The use of methanol as a motor fuel has been discussed repeatedly since the 1920s. Use has so far been restricted to high-performance engines for racing cars and airplanes. The combustion of methanol in four-stroke engines has been investigated for a long time. Methanol has been found to be an ideal fuel in many respects. Because of its high heat of vaporization and relatively low calorific value, a substantially lower combustion chamber temperature is achieved than with conventional motor fuels. Emissions of nitrogen oxides, hydrocarbons, and carbon monoxide are

**Table 4.** Comparison of methanol and a typical fuel (gasoline) for use in Otto engines

| Property | Gasoline | Methanol |
| --- | --- | --- |
| Density, kg/L | 0.739 | 0.787 |
| Calorific value, kJ/kg | 44 300 | 22 693 |
| Air consumption, kg/kg | 14.55 | 6.5 |
| Research octane number | 97.7 | 108.7 |
| Motor octane number | 89 | 88.6 |
| Mixed research octane number | | 120–130 |
| Mixed motor octane number | | 91–94 |
| Reid vapor pressure, kPa | 64 | 32 |
| Boiling point range, °C | 30–190 | 65 |
| Heat of vaporization, kJ/kg | 335 | 1174 |
| Cooling under vaporization with stoichiometric amount of air, °C | 20 | 122 |

lower. This is offset, however, by increased emission of formaldehyde.

The important properties of methanol for use as a fuel are compared with those of a conventional fuel (gasoline) in Table 4. Consumption is higher because of the lower calorific values.

Methanol can be used in various mixing ratios with conventional petroleum products:

M 3    Mixture of 3% methanol with 2–3% solubilizers (e.g., isopropyl alcohol) in commercially available motor fuel. This system is already widely used because modification of motor vehicles and fuel distribution systems is not required.

M 15   Mixture of 15% methanol and a solubilizer with motor fuel; alterations to the motor vehicles are necessary in this case. The proposed use of M 15 to increase the octane number in unleaded gasoline has been supplanted by the large increase in the use of MTBE.

M 85   Methanol containing 15% $C_4$–$C_5$ hydrocarbons to improve cold-start properties. Modified vehicles and fuel distribution systems are necessary.

M 100  Pure methanol: Vehicles must be substantially modified and fully adapted to methanol operation.

The necessary modifications for methanol operation involve the replacement of plastics used in the fuel system (see Section 6.2). The ignition system and carburetor or fuel injection unit also have to be adapted. With M 85 and M 100 the fuel mixture must be preheated because vaporization of the stoichiometric amount of methanol in the carburetor results in a cooling of 120 K.

In mixtures with a low methanol content (M 3, M 15) phase separation in the presence

of traces of water must be avoided. Dry storage, transportation, and distribution systems must be available for mixed fuels to prevent separation of water–methanol and hydrocarbon phases.

A further restriction on the use of methanol in gasoline is imposed by the increase in gasoline vapor pressure (Reid vapor pressure, RVP). In some warm regions of the United States, legal restrictions on the RVP have already been introduced to reduce hydrocarbon emissions, which are an important factor in the formation of photochemical smog and increased ozone concentration in the lower atmosphere. As a result, methanol can no longer be added to motor fuel because it increases the vapor pressure of the butane used as a cheap octane booster.

Nevertheless, methanol has proven its ability to be used as sulfur-free alternative fuel in fleet tests for passenger cars, buses, and trucks.

***Methanol as Diesel Fuel.*** Exclusive operation with methanol is not possible in diesel engines because the cetane number of methanol is three and methanol will therefore not ignite reliably. Thus, methanol has to be converted into the downstream product DME, which is considered an excellent alternative to diesel.

When converted with suitable fats and oils, methanol yields fatty acid methyl esters (FAMEs), also called biodiesel ($\rightarrow$ Automotive Fuels, Section Fatty Acid Methyl Esters). In 2011, 6% of total methanol produced worldwide was used for biodiesel production. The biodiesel production is expected to increase further, especially in the emerging economies of South America [188]. However, due to its properties, diesel blends with more than 7% biodiesel are unlikely to be introduced for conventional diesel engines [189]. This will probably lead to a decrease of growth rates during the next decade [188]. In addition, today's technologies for biodiesel production are mainly based on vegetable oils, such as sunflower, soybean, rapeseed, or palm oil and are thus in competition with food production.

***Other Energy Uses of Methanol.*** A use that has been discussed particularly in the United States and implemented in pilot projects is the firing of peak-load gas turbines in power stations (peak shaving). Benefits include simple storage and environmentally friendly combustion in the gas turbine.

Methanol as well as DME has been demonstrated to be a possible future fuel for stationary turbine engines [190]. The use of methanol as a fuel in conventionally fired boilers obviates the need for costly flue gas treatment plants but is not yet economically viable.

The gasification of methanol to obtain synthesis gas or fuel gas has often been proposed. Apart from exceptions, such as the production of town gas in Berlin, here too, economic problems have prevented technical implementation.

However, the chemical conversion of $CO_2$ into methanol using hydrogen produced by water electrolysis is widely regarded as one possibility to produce renewable fuels or to use methanol as a liquid energy carrier. Although the ideas are not new and have already been published [191–193], this approach gains more acceptance and is currently under investigation.

## 9.3. Other Uses

Methanol's low freezing point and its miscibility with water allow it to be used in refrigeration systems, either in pure form (e.g., in ethylene plants) or mixed with water and glycols. It is also used as antifreeze in heating and cooling circuits. Compared to other commonly used antifreezes (ethylene glycol, propylene glycol, and glycerol), it has the advantage of lower viscosity at low temperature. It is, however, no longer used as engine antifreeze; glycol-based products are employed instead.

Large amounts of methanol are used to protect natural gas pipelines against the formation of gas hydrates at low temperature. Methanol is added to natural gas at the pumping station, conveyed in liquid form in the pipeline, and recovered at the end of the pipeline. Methanol can be recycled after removal of water taken up from natural gas by distillation.

Methanol is also used as an absorption agent in gas scrubbers. The removal of $CO_2$ and $H_2S$ with methanol at low temperature (Rectisol process, Linde and Lurgi) has the advantage that traces of methanol in the purified gas do not generally interfere with further processing [194].
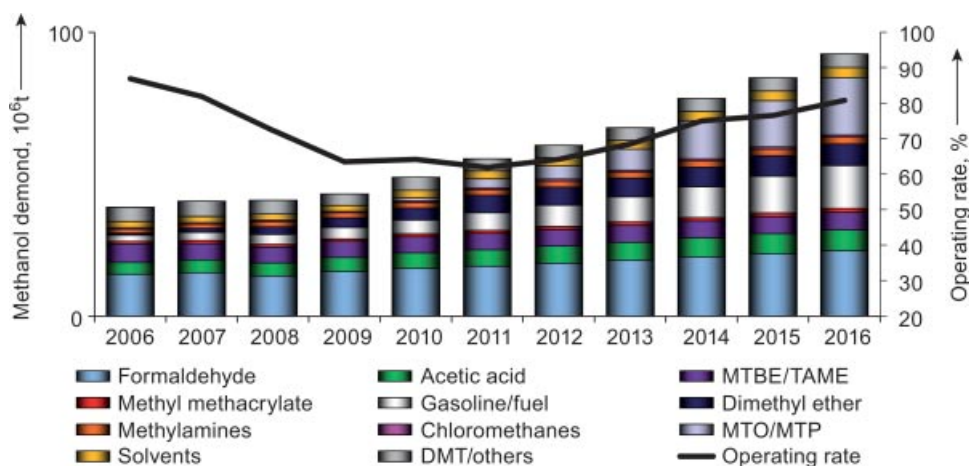
**Figure 7.** World methanol demand from 2006 projected until 2016, adapted from [196]
TAME = *tert*-amyl methyl ether—Operating rate

The use of pure methanol as a solvent is limited, although it is often included in solvent mixtures.

## 10. Economic Aspects

*Economics of Methanol Production.* The costs of methanol production depend on many factors, the most important being direct feedstock costs, investment costs, and costs involved in logistics and infrastructure.

Natural gas, naphtha, heavy heating oil, coal, and lignite are all used as feedstocks in methanol plants. In heavy oil-based plants and to an increasing extent in coal-based plants the principal cost burden is accounted for by capital costs. Under present conditions, the balance between investment and operating costs clearly favors natural gas-based plants. All large plants currently being built or planned are designed for use with natural gas. The exception is China where coal is the feedstock of choice for production of chemical commodities. The Chinese chemical industry plans to install plants with up to $50 \times 10^6$ t/a methanol capacity until 2015 that are completely based on coal [195].

*Methanol on the World Market.* After ammonia, methanol is quantitatively the largest product from synthesis gas. Worldwide capacity in 1988 was $19 \times 10^6$ t. In 2010, $46 \times 10^6$ t of methanol was produced worldwide. The mean annual production growth rate is about 9%. The worldwide methanol demand starting from 2006 and projected until 2016 is illustrated in Figure 7 [196].

The methanol industry underwent radical structural changes during the 1980s. Previously, companies that consumed large quantities of methanol produced the compound themselves from the most readily accessible raw materials at the site of use (i.e., highly industrialized countries with expensive energy sources). Since then the number of plants that produce methanol at remote sites exclusively for sale to processors has risen dramatically.

After the energy crisis of the 1970s, intensive oil prospecting led to the discovery of large natural gas fields in many remote regions. Because little demand for natural gas existed in these regions, the relevant countries in South America, Asia, and the Caribbean were interested in selling natural gas as such or in another form to industrialized countries.

Another, hitherto little-used energy source is the associated gas, which is still often flared off. In addition to the transportation of liquefied methane and its use as a starting material for ammonia production, methanol production is often the most suitable alternative for marketing such gases. The technology of methanol production is relatively simple, and transport and storage involve inexpensive technology. On the basis of these considerations, new large-scale

natural gas-based plants producing methanol for export were built. The largest single train natural gas-based plants in operation have a capacity of 5 000 t/d. Plants in operation with capacities above 5 000 t/d use coal or have supplemental feedstocks, such as carbon dioxide or purge gas from other plants. Nevertheless, all main licensors, such as Lurgi, Johnson Matthey, and Haldor Topsøe publish and design plants up to 10 000 t/d single train methanol capacities. As a consequence of this development, older methanol plants in industrialized countries, such as the United States, Japan, and Germany have been shut down. Because there is no longer a close relationship between supply and demand, large price fluctuations occur, which are hardly justified by actual market conditions. This makes long-term price forecasts impossible and increases economic risks for new projects.

# 11. Toxicology and Occupational Health

## 11.1. GHS Specifications

Within the actual safety regulations for hazardous components, the following hazard statements (H) are valid for liquid methanol: H225, H301, H311, H331, H370. These H statements replace the formerly valid statements R11, R23/24/25, and R39/23/24/25. The respective precautionary statements (P) are P210, P233, P280, P303+361+353, P304+340, and P301–310. These statements are replacing the formerly valid statements S01/02, S07, S16, S36/37, and S45.

More detailed information is given by the Methanol Institute [179].

## 11.2. Toxicology

*Human Toxicology.* The first accounts of the poisonous action of "methylated spirits" were published in 1855 [197]. However, the number of cases of poisoning increased only after the production of a low-odor methanol. In 1901, DE SCHWEINITZ reported the first cases of industrial poisoning [198].

Liquid methanol is fully absorbed via the gastrointestinal tract [199] and the skin [200] (absorption rate, 0.19 mg cm$^{-2}$ min$^{-1}$). Methanol vapor is taken up in an amount of 70–80% by the lungs [201]. The compound is distributed throughout body fluids and is largely oxidized to formaldehyde and then to formic acid [202]. It is eliminated unchanged through the lungs [200] and in the urine. Elimination half-life is ca. 2–3 h.

The metabolism of methanol to formic acid in humans and primates is catalyzed by the enzyme alcohol dehydrogenase in the liver. This enzyme can be inhibited competitively by ethanol. Formic acid is oxidized to carbon dioxide and water in the presence of folic acid. Because folic acid is not available in sufficient amount in primates, formic acid may accumulate in the body. This leads to hyperacidity of the blood (acidosis), which is ultimately responsible for methanol poisoning [202].

The symptoms of methanol poisoning do not depend on the uptake route (percutaneous, inhalational, oral) and develop in three stages. An initial narcotic effect is followed by a symptom-free interval lasting 10–48 h. The third stage begins with nonspecific symptoms, such as abdominal pain, nausea, headache, vomiting, and lassitude, followed by characteristic symptoms, such as blurred vision, ophthalmalgia, photophobia, and possibly xanthopsia. Depending on the amount of methanol, individual sensitivity, and the time when treatment is initiated, visual disturbances can either improve or progress within a few days to severe, often irreversible impairment of sight or even to blindness [203–206]. The symptoms are accompanied by increasing hyperacidity of the blood due to the accumulation of formic acid, with disturbances in consciousness, possibly deep coma, and in severe cases, death within a few days. The lethal dosage is between 30 and 100 mL/kg body weight. Sensitivity to methanol varies widely. Cases have been reported in which no permanent damage occurred after drinking relatively large amounts of methanol (200 or 500 mL) [207, 208]; in another case, however, irreversible blindness resulted after consumption of 4 mL [209].

The treatment of acute oral methanol poisoning [204] should be initiated as quickly as possible with the following measures:

1. Administration of ethanol: In suspected cases of methanol poisoning, 30–40 mL of ethanol (e.g., 90–120 mL of whiskey) is administered immediately as a prophylactic before the patient is referred to a hospital. Because ethanol has a greater affinity for alcohol dehydrogenase than methanol, oxidation of methanol is inhibited; the production of formaldehyde and formic acid from methanol is thus suppressed.
2. Gastric lavage
3. Hemodialysis
4. Treatment with alkali: Sodium bicarbonate is infused to control blood hyperacidity.
5. Administration of CNS stimulants (analeptics)
6. Drinking larger volumes of fluid
7. Eye bandage: The eyes should be protected against light
8. The patient should be kept warm

Methanol has a slight irritant action on the eyes, skin, and mucous membranes in humans. Concentrations between 1 500 and 5 900 ppm are regarded as the threshold value of detectable odor.

Chronic methanol poisoning is characterized by damage to the visual and central nervous systems. Case histories [210, 211] have not been sufficiently documented; whether poisoning is caused by chronic ingestion of low doses or ingestion of intermittently high (subtoxic) amounts is uncertain.

***Animal Toxicology.*** Experiments on animals have shown that methanol does not cause acidosis or eye damage in nonprimates (e.g., rats, mice). It generally has a narcotic, possibly lethal, effect. Investigations on laboratory animals cannot, therefore, be extrapolated to humans, at least in the higher dosage range.

In a study on reproductive toxicology, methanol was administered to rats by inhalation during pregnancy. No embryotoxic effects were found after exposure to 5 000 ppm [212]. The authors conclude that observance of the recommended concentrations (MAK or TLV values) offers sufficient protection against fetal abnormalities in humans.

In the Ames test, the sex-linked lethal test on *Drosophila melanogaster* and the micronucleus test in mice, methanol was not mutagenic [213, 214].

## 11.3. Occupational Health

No special precautions need be taken when handling methanol because it is not caustic, corrosive, or particularly harmful environmentally. If methanol is released under normal conditions, no danger exists of buildup of acutely toxic concentrations in the atmosphere. (Chronic poisoning via the respiratory tract or oral ingestion is described in Section Human Toxicology) However, absorption through the skin does constitute a danger, and methanol should be prevented from coming in direct contact with skin.

Appropriate workplace hygiene measures should be adopted if methanol is handled constantly. Rooms in which methanol is stored or handled must be ventilated adequately. The TLV–TWA value (skin) is 200 ppm (262 mg/m$^3$), and the TLV–STEL value is 250 ppm (328 mg/m$^3$). The MAK value is 200 ppm (270 mg/m$^3$). Gas testing tubes can be used to measure the concentration in air. The peak limit should correspond to category II, 1: i.e., the MAK value may be exceeded by a maximum of 100% for 30 min, four times per shift [215]. Respirators must be worn if substantially higher concentrations are present. Filter masks (filter A, identification color brown) can be used only for escape or life-saving purposes because they are exhausted very quickly. Respirators with a self-contained air supply and heavy-duty chemical protective clothing should be used for longer exposures to high methanol concentrations (> 0.5 vol%).

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