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Methanol as an Energy Carrier

**Peter Biedermann, Thomas Grube,
Bernd Höhlein (Hrsg.)**

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Anglo-Saxon units of measurement

The Anglo-Saxon units of measurement commonly used in the respective subject area have not been converted into the SI system, but conversion and estimation aids are provided.

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Preface

The present volume is based on volume 28 “Methanol als Energieträger” (Methanol as an Energy Carrier) published in the Energy Technology series in 2003 (ISBN 3-89336-338-6). It has above all been supplemented by additional contributions to the chapters on DMFC and methanol preparation:

– DMFC (Chapter 3)
– Synthesis gas (Chapter 5)
– Process engineering of methanol synthesis (Chapter 6)
– Methanol and MCFC (Berlin project) (Chapter 11.3)

The chapters of the 2003 editon have been updated. However, this was not possible in each case for costs or prices because of the dramatic price increases at the end of 2005.

The editors would like to thank Ms M. Heinz from the Language Service at the Central Library of Research Centre Jülich for the translation of the German text into English and for useful advice.

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0.2 Abstract

For the future, a strongly growing energy demand is expected in the transport sector worldwide. Economically efficient oil production will run through a maximum in the next decade. Higher fuel prices and an environmentally desirable reduction of emissions will increase the pressure for reducing fuel consumption and emissions in road traffic. These criteria show the urgent necessity of structural changes in the fuel market.

Due to its advantages concerning industrial-scale production, storage and global availability, methanol has the short- to medium-term potential for gaining increased significance as a substitution product in the energy market. Methanol can be produced both from fossil energy sources and from biomass or waste materials through the process steps of synthesis gas generation with subsequent methanol synthesis.

Methanol has the potential to be used in an environmentally friendly manner in gasoline/methanol mixtures for flexible fuel vehicles with internal combustion engines and in diesel engines with pure methanol. Furthermore, it can be used in fuel cell vehicles with on-board hydrogen production in direct methanol fuel cell drives, and in stationary systems for electricity and heat generation as well as for hydrogen production. Finally, in portable applications it serves as an energy carrier for electric power generation.

In this book, the processes for the production and use of methanol are presented and evaluated, markets and future options are discussed and issues of safety and environmental impacts are addressed by a team of well-known authors.

1 Introduction

Methanol as a chemical raw material has long been a marketable product. About 15–20 years ago, however, Californian initiatives already aimed at minimizing traffic-induced smog situations especially in Southern California by the use of clean energy carriers such as methanol. This has led to considerations and initial attempts to provide filling stations for methanol/gasoline mixtures (85/15) and correspondingly adapted Otto engines for the market. Since the automobile market is oriented globally, there have been relevant activities worldwide and thus also in Germany with the first filling stations and vehicles. In the 1990s, these efforts were not further pursued, but instead methanol became a potential fuel for fuel cell vehicles (FCVs) in combination with on-board reformers for hydrogen production. A first filling station for FCVs was built within the framework of the California Fuel Cell Initiative and the first vehicles, such as Daimler-Chrysler's “NECAR 5”, were developed and put on the road.

Methanol as an energy carrier for road traffic involves the following criteria: lower tank-to-wheel emissions, producible from fossil and biomass-based primary energies, handling of a normally liquid energy carrier with known infrastructures and safety constraints. These criteria are important for building up future energy supply structures for globally increasing transport and traffic along with fewer oil-based fuels and more synthetically produced fuels including also methanol.

1.1 Fuel supply for the transport sector

For the future, a strongly growing energy demand is expected in the transport sector, which will still largely be covered by crude oil coming mainly from the Middle East. Economically efficient oil production will run through a maximum in the next decade. This situation of future fuel supply is likely to produce instabilities in ecological, economic and political respects. Expanding natural gas markets will in future primarily have to make use of the great reserves in the Middle East (Iran, Qatar, Saudi Arabia) and the Russian Federation [SCHMITZ 2002]. Higher fuel prices and an environmentally desirable reduction of traffic-induced climate-relevant and locally effective emissions with their secondary pollutants will increase the pressure for reducing fuel consumption and emissions in road traffic. The essential motivation for the envisaged structural changes in the transport sector can be defined as follows:

– improvement of local and regional air quality,
– restricting global warming,
– less dependence on oil.

These changes will have to be accomplished by an increase in the efficiency of "clean" drive systems and a market launch of fuels with sufficient economical availability, which – including their use in motor vehicles – will contribute towards reducing the emissions in the transport sector.

Future fuel supply is evaluated according to the following criteria:

– availability and range of energy carrier resources (fossil / renewable),
– infrastructure requirements,
– evaluation of fuel supply in terms of energy,
– pollutant and greenhouse gas emissions of the full fuel cycle (local / regional / global),
– potential for forming secondary pollutants,
– fuel supply costs,
– fuel specifications,
– impacts on safety, environment, health and acceptance.

In the medium- to long-term perspective, new final energy carriers for motor vehicles will be produced on a fossil and increasingly on a renewable basis. In order to utilize them – in addition to further developed internal combustion engines – hybrid vehicles, electrically driven battery vehicles and electrically driven fuel cell vehicles will also have to be taken into consideration in future.

Final energy carriers, which can be simultaneously used both for conventional drives and for new drives with fuel cells and which in the long term are produced on the basis of renewable sources of primary energy, will have good prospects for future application. An increased incorporation of renewable energy sources in the future presupposes adequate availability at competitive costs and the creation of new infrastructures [EDINGER/ISENBERG/HÖHLEIN 2003].

Figure 1 shows possible pathways of future fuel supply on a synthesis gas (syngas) basis. Natural gas or associated gas, coal and biomass are suitable feedstocks for the production of synthetic liquid energy carriers. Subsequently to a synthesis gas (H_2, CO, CO_2) production process, Fischer-Tropsch diesel, methanol or hydrogen or substitute natural gas (SNG) can be produced.

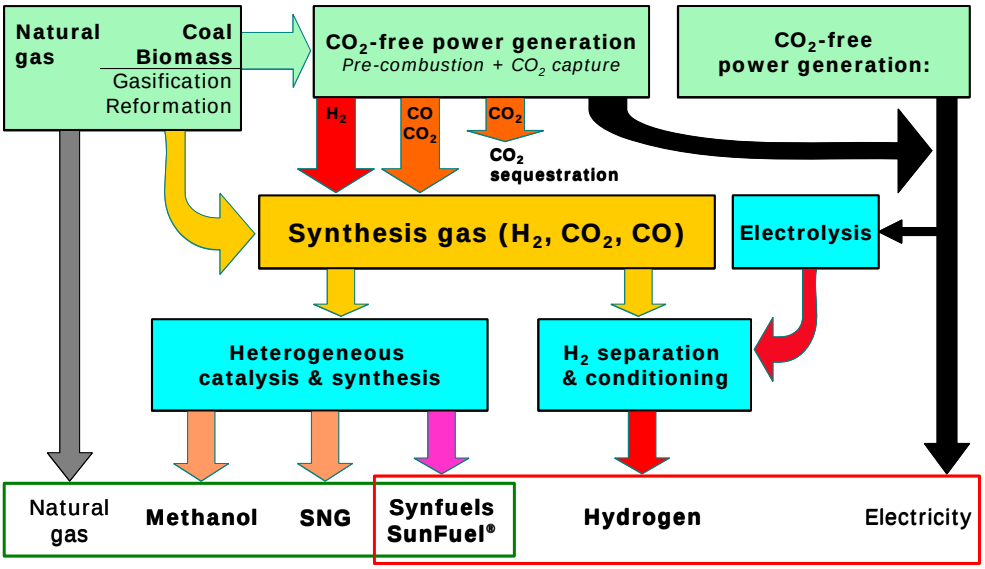


Figure 1: Synthesis gas derived alternative fuels from fossil and renewable sources

This would require new production capacities and for methanol and hydrogen also new infrastructures. The production of these energy carriers is also possible on the basis of biomass. One then speaks of biomass-to-liquid (BTL) or SunFuel® for synthetic liquid fuels in addition to vegetable oil methyl esters (FAME) and bioalcohols (ethanol). A use of synthetic energy carriers based on synthesis gas is basically possible in both combustion-engine and fuel-cell drives.

Due to its advantages concerning industrial-scale preparation, storage and global availability, methanol and also synthetic liquid fuels have the short- to medium-term potential for gaining increased significance as a substitution product in the energy market.

1.2 Global situation of methanol

Traditionally, methanol is a chemical base material mainly produced from natural gas today and forms the basis for the production of formaldehyde, MTBE and acetic acid; these three products cover about two thirds of the total methanol demand.

The synthesis gas produced from natural gas, coal or biomass opens up prospects for new production possibilities of methanol and new products

such as synthetic fuels, hydrogen and indirectly also electricity (**Figure 1**).

These prospects and the well-founded interest in their further development have meanwhile led to various pilot plants aiming at a future commercialization and enhancement of these technologies.

At present, there is still a lack of goal-oriented driving forces in the market enabling further implementation. The dominance of oil and the associated trends in the market constitute a barrier that is difficult to overcome.

We can at present only take a stance on the development of prices for the traditional chemical application of methanol. Pricing will probably change fundamentally if methanol were to become an energy carrier one day.

The demand for methanol grows with the gross national product (GNP). This basic experience plays an essential role in demand coverage and thus in the estimation of prices.

2003 production capacities amount to 36.7 million tons worldwide. This figure reflects the nominal capacity; real production is in the range of 85% (historical average of capacity utilization) of this capacity value. Modern plants are definitely able today to increase this output to 90% or more.

The global demand for the calendar year 2004 was approx. 34 million tons compared to a production of approx. 33 million tons. Even if certain stocks are included, a bottleneck in the availability of methanol must be expected. This is due to the fact that in the past two years no new production capacity has come onto the market. The price level has developed accordingly; methanol is currently experiencing an unparalleled historical boom.

The new and first methanol megaplant with a nameplate capacity of 1.65 million tons located in Trinidad started production in quarter 3 of 2004, however with some technical difficulties, which were solved over 2005. It is to be expected that this plant will reach full capacity throughout 2006.

In October 2005 another site with 2.0 million tons came on stream in Trinidad, working sufficiently from the very beginning.

In 2005 and 2006 prices for methanol were still soaring because of tightness of production. The new plants were not able to compensate the closures of older and ineffective working plants. The exploded high gas prices led one European producer with a capacity of approx. 950,000 MT per year to unexpectedly close the plant by mid-2006, having reduced production effectively by 50% by quarter 4 of 2005.

Due to the reduction of MTBE production, approx. 2.5 million tons of methanol will be additionally available on the world market in the same period.

However, these volumes became free step by step und were nearly all swallowed by annual global demand increasing by 4–5% in that period, especially by permanently increased consumption in China.

In 2007 and thereafter a relaxation of the market is expected, because then some new capacity will start production located in Iran, China and Saudi Arabia, followed by investments in Oman. 6.0–6.5 million tons of additional methanol are expected to be probably available to the consumer up to 2008.

It is remarkable to note that investments in increasingly larger plants are being made. Today's megaplant of 1.65 million tons capacity per year (5,000 tons per day) is becoming a standard. The first plant of this type is named Atlas, is located in the Caribbean and is just about to go into operation. Another plant of this design was to follow in Iran in 2005 (LURGI).

The published investment activities will lead to a change of the flow of commodities/supplies of methanol on the world market.

In the Caribbean, where approximately 2.8 million tons of methanol were produced in 2004, new plants will increase the output to approx. 6.5 million tons per year. In Chile, 4 million tons will then be produced instead of 3 million tons per year today.

This means that approximately 3.5 million tons of methanol will be additionally produced in the logistically favourable neighbourhood of America. On the American mainland, in contrast, those production facilities are located which are unprofitable even today due to the development of the gas costs. These plants are threatened with closure, and there is a closure potential of as much as 3.5 million tons in total.

Great attention must be paid to the investments in the eastern part of the world. Oman, Qatar, Saudi Arabia and above all Iran could in total produce approx. 15 million tons of methanol in 2010 compared to a capacity of approximately 6 million tons today. However, due to new estimates it could be possible that not all expected new capacity will become commercial and available for the market. It has to be admitted that the investments, especially the capacities in Iran, could also be used for captive application and DME. This possible local consumption will reduce the volume for commercialization.

Owing to these new capacities, both Europe and the Asian area can be supplied much more favourably than is the case today due to new logistic challenges and efforts.

All the new production facilities have a lot in common; they produce methanol where the gas deposit is located and they have favourable gas conditions in the long term that ensure a profitable production of methanol in the long term.

Table 1: Global methanol supply and demand 2005–2008, quantities / million tons [DE WITT 2006]

	2005	2006 [1]	2007 [1]	2008 [1]
Global supply				
new capacity	4.4	4.1	6.4	7.7
Total capacity	44.0	48.1	54.5	62.2
Estimated supply	42.0	44.8	51.0	55 ?
Global demand				
new demand China	0.95	0.8	0.6	0.6
new demand others	0.97	1.0	1.1	1.2
MTBE curtailments	0.3	-0.8	-1.2	?
Total demand	34.5	35.5	36.0	37.8
Utilization rate / %	82.1	79.2	70.6	68.7

[1] estimates

But none of these facilities will suffice to produce and supply the quantities required if syngas/methanol were to play an increasing role as a new energy source for road traffic one day.

Extraordinarily new was heard from China in regard of using methanol as a fuel. In the province of Shanxxi there are fundamental plans to produce 20 million tons of methanol per year based on coal gasification technology for transportation [DE WITT 2006].

Finally **Table 1** gives an overview of the (estimated) global methanol supply and demand for the period 2005 to 2008.

1.3 Summary of Chapter 1

Methanol as an energy carrier for road traffic involves criteria like lower tank-to-wheel emissions, producible from fossil and biomass-based primary energies and a handling of a normally liquid energy carrier with

known infrastructures and safety constraints. For the future, a strongly growing energy demand is expected in the transport sector. Higher fuel prices and an environmentally desirable reduction of traffic-induced climate-relevant and locally effective emissions with their secondary pollutants will increase the pressure for reducing fuel consumption and emissions in road traffic. These challenges will have to be met by an increase in the efficiency of “clean” drive systems. In the medium- to long-term perspective, new final energy carriers for motor vehicles will be produced on a fossil and increasingly on a renewable basis.

Natural gas or associated gas as well as coal or biomass are suitable via synthesis gas for the production of synthetic liquid energy carriers – Fischer-Tropsch diesel as synfuel, methanol or hydrogen or for substitute natural gas. This would require new production capacities and for methanol and hydrogen also new infrastructures. These energy carriers can also be produced on the basis of biomass. One then speaks of biomass-to-liquid (synthetic) fuels. A use of synthetic energy carriers is basically possible in both combustion-engine and fuel-cell drives.

Traditionally, methanol is a chemical base material mainly produced from natural gas today and forms the basis for the production of formaldehyde, MTBE and acetic acid; these three products cover about two thirds of the total methanol demand. Synthesis gas produced from natural gas, coal or biomass opens up prospects for new production possibilities of methanol and new products such as synthetic fuels, hydrogen and indirectly also electricity. These prospects and the well-founded interest in their further development have meanwhile led to various pilot plants.

The demand for methanol grows with the gross national product. This basic experience plays an essential role in demand coverage and thus in the estimation of prices. At present we only can take a stance on the development of prices for the traditional chemical application of methanol. Pricing will probably change fundamentally if methanol were to become an energy carrier one day.

In 2005 and 2006 prices for methanol were still soaring. High gas prices exploded. MTBE production was reduced. China shows a permanently increasing consumption. In 2007 and thereafter a relaxation of the market is expected.

Investments in increasingly larger plants are being made but it could be possible, that not all expected new capacity will become commercial and available for the market. All the new production facilities produce metha-

nol where the gas deposit is located and they have favourable gas conditions in the long term.

None of these facilities will suffice to produce and supply the quantities required if syngas/methanol were to play an increasing role as a new energy source for road traffic one day.

2 Possible energy carriers for road traffic

From the analysis of the interrelation of energy use and environmental impacts, the following statements can be derived concerning the energy carriers for road traffic:

– Road traffic mainly causes emissions of carbon monoxide (CO), hydrocarbons (C_nH_m) and nitrogen oxides (NO_x) and is thus also responsible for the formation of summer smog (ozone, formaldehyde and other secondary pollutants).
– The increasing introduction of three-way catalytic converters for passenger cars reduces the legally regulated emissions from passenger cars, but not those from commercial vehicles; problematic local / regional immission areas are still possible. CO_2 emissions from traffic are rising.
– Various measures in fuel and engine technology are suitable to improve the conventional drive systems in road traffic and thus quantitatively reduce the emissions polluting the environment.
– A great potential for emissions reduction is provided by new energy carriers such as natural gas, methanol (CH_3OH) and ethanol (C_2H_5OH), which in the same way as gasoline and diesel emit NO_x, CO and C_nH_m during engine combustion.
– Systems of novel energy carriers and power trains in conjunction with efficient energy conversion can also improve the quality of emissions and thus reduce the potential for forming secondary pollutants (ozone and others).
– Novel energy carriers must be compared with respect to specific energy consumption and specific emissions of CO, carbon dioxide (CO_2), NOx, C_nH_m, formaldehyde (CHOH), particulate and sulphur as well as the potential for forming secondary pollutants for the full fuel cycle from primary energy source up to the moving car.
– On the basis of natural gas or feedstocks from petrochemistry, waste management or agriculture (so-called secondary biomass) fuels such as hydrogen (H_2), methanol and Fischer-Tropsch diesel can be produced from synthesis gases (major components CO, CO_2, H_2); they can play a special role in future fuel supply.
– In the long term, hydrogen can be supplied on a renewable basis not only for internal combustion engines but also, in particular, for more efficient fuel cell power trains.

– Another highly regarded biofuel is ethanol which, for economic reasons, is available on the transport energy market in Brazil (1990: 88% of all new passenger cars for ethanol operation [BRASIL 2000]). Ethanol is also suited as a blend component (E5) or for the production of ETBE for fuels.
– Under certain regional circumstances, ethanol produced by the fermentation of biomass can also be used for internal combustion engines (cf. Brazil).
– Methanol can be used in flexible fuel vehicles (FFV), gasoline engines (M85), diesel engines (M100) and fuel cell power trains and/or also for methyl (tertiary) butyl ether production as octane booster or gasoline blend (M3).
– The most important properties of methanol are as follows: The molecule (CH_3OH) is simply structured; it has a very low carbon/hydrogen ratio. Methanol is liquid at ambient temperature. The mass/volume-related energy density of the tank system is about 46%/46% for a tank system for gasoline and 200%/300% for a tank system for liquid hydrogen ($L.H_2$). Methanol has a corrosive effect on the materials of tanks, pipes and fittings; it is biodegradable (cf. **Chapter 4**). Hydrogen can be produced by reforming methanol at 250 °C (cf. **Chapter 6.6**).
– Methanol can be produced from natural gas (or coal, oil, biomass, waste materials) via the production of synthesis gas with subsequent methanol synthesis. It can then be used in internal combustion engines or also directly (cf. **Chapter 3.4**) or indirectly in fuel cells for producing electricity for electric drives. For indirect use in fuel cells, a reformer is necessary for “on-board hydrogen production” (for the function of fuel cells cf. [STOLTEN et al. 2002]).
– The provision of methanol as a final energy carrier on a renewable basis greatly depends on local and regional possibilities and needs.

2.1 Costs and emissions

The specific costs (per energy content of the energy carrier) for the provision of different primary and secondary or final energy carriers that are ultimately used in road traffic are compiled in **Table 2**.

Figure 2 shows the dependency between specific greenhouse gas emissions and specific fuel costs. The specific costs (per energy content of the energy carrier) in Germany for the provision of different primary and sec-

ondary or final energy carriers that are ultimately used in road traffic are compiled in **Table 3** and the specific taxes in **Table 4**.

Table 2: Analysis of energy carrier costs (2000–2003)

Energy carrier	Costs / (US-$/GJ$_{energy\ carrier}$)
Methanol (NG 1) 2 [MPE 2000]	5–7 (NG:1.5–2.5 for 2,000 t/d)
Methanol / FOB 3 [HODGES 2002]	13–5 (1/2000–9/2002)
Methanol (remote gas) 2 [LURGI 2000], [LIEBNER 2002]	4 and 5 (remote gas: 0.5 and 0.7), respectively; (10 kt/d)
Methanol (biomass) 2 [SPECHT 2002]	16–28
H_2 (NG) 2 [ULLMANN 2003]; (300 MW_{H2}, s. [DREIER 2000])	9 (NG: 4)
C.H_2 4 (NG) 2 at filling station [ADL 2000]	17 (NG: 4)
H_2 (biomass / coal) 2 [PU 1996]	15 (biomass: 2 / coal: 1.3; + 2 for sequestration)
H_2 (electrolysis) 4 at filling station [PU 1996]	25 (renewable electricity: 12.5)
C.H_2 5 (electrolysis, wind power) 4 [ARAL 2001]	46 (2010–2020)
H_2 (electrolysis, electricity D) 4 at filling station [VALENTINE 2001]	47 (50% substitution in Germany)
L.H_2 6 or C.H_2 (NG) 2 at filling station [VALENTINE 2001]	21 (50% substitution in Germany)
ethanol 7 [CEA 2003]	21 / 19 / 15 (2000 / 2005 / 2010)

Conversions: 1 GJ = (100/0.36) kWh; 1 US-$/GJ = 0.36 US-Cent/kWh; 1 € = 1 US-$; 1 NG = natural gas; 2 gasification / reforming of the energy carrier); 3 FOB = free on board Rotterdam; 4 water electrolysis; 5 C.H_2 = compressed hydrogen with delivery to filling station; 6 L.H_2 = liquid hydrogen; 7 in France

The Transport Energy Strategy (TES) (an initiative of the German industry in coordination with the Federal Government) has set itself the aim of developing and implementing a strategy for the medium-term nationwide market introduction of an alternative fuel for transport and traffic [TES 2001]. This goal is based on the TES vision of a sustainable energy supply, which will reduce environmental pollution and conserve raw material reserves. From a broad range of 10 potential alternative fuels and over 70

supply pathways, TES selected three fuels for further consideration: natural gas, methanol and hydrogen.

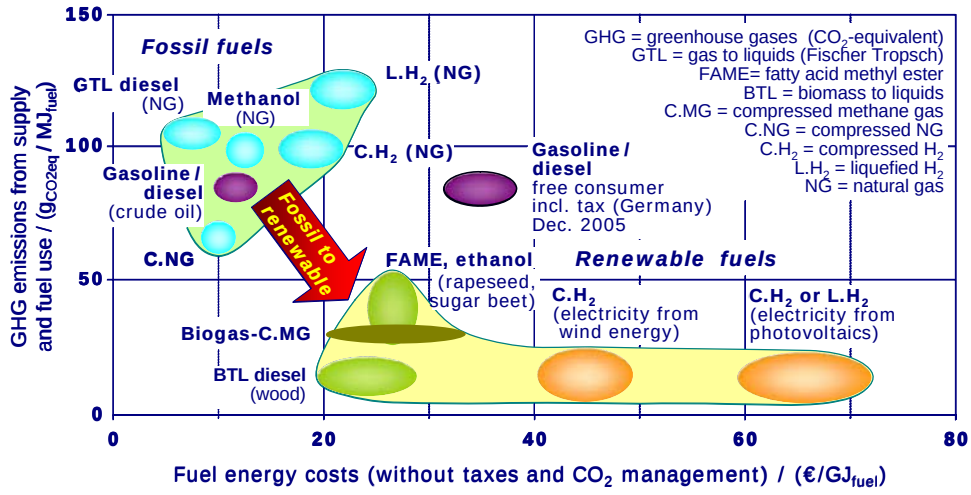


Figure 2: Fuel energy costs and greenhouse gas emissions

Table 3: Specific fuel costs in Germany

Energy carriers	Specific costs / (€ / GJ)	Remarks / Taxes [1]
Gasoline (at filling station, 2005/07) (gasoline, FOB [2])	37 10	Incl. (EnerTax/EnvirTax +VAT) (for comparison only)
Diesel (at filling station, 2005/07) (diesel, FOB [2])	30 10	Incl. (EnerTax/EnvirTax +VAT) (for comparison only)
RME [3] (vehicle fleet [4], 2004) (RME, FOB, 2005)	21 29	Without PetroTax, incl. VAT (for comparison only)
Bioethanol (EU market) (Bioethanol, FOB, 2005)	15–24 25	Without PetroTax, incl. VAT (for comparison only)
Biogas (C.MG [5], NRW, 2005)	8–22	Without taxes
C.NG [6] (at filling station, 2005)	14–17	Incl. (EnerTax/EnvirTax +VAT)
H_2 from NG [7] at filling station (NG: 6)	20–23	Net of taxes [Linde 2004] @ 50% fuel substitution by H_2

[1] AlcoTax = tax on alcohols; EnerTax = energy tax; EnvirTax = environmental tax; PetroTax = petroleum tax; VAT = added value tax. [2] FOB = free on board Rotterdam; [3] RME = rape oil methyl ester; [4] 8,000 l/month; [5] C.MG = compressed methane gas; [6] C.NG = compressed NG; [7] NG = natural gas

Possible energy carriers for road traffic

Table 4: Specific fuel taxes in Germany without VAT (of early 2003)

Energy carriers: (EnerTax + *EnvirTax*) [1]	Specific taxes / (€ / GJ)	Remarks
Gasoline: (50 + *15*) cent/l	20	S [6] < 10 mg/kg
Diesel: (32 + *15*) cent /l	13	S < 10 mg/kg
LPG [2]: (16.1 + *0*) cent /kg	3.5	Up to y2020
NG [3] (vehicle): (1.39 + *0*) cent /kWh_{HHV}	3.8	Up to y2020
H_2 (from NG): (0 + *0*)	3.8	
H_2 (from biomass): (0 + *0*)	0	
RME [4]: (0 + *0*)	0	
NG (heating): (0.18 + *0.16*) cent /kWh_{HHV}	1	
Heating oil EL [5] (heating): (4 + *2*) cent /l	1.6	
Electricity: (2.05 + *0*) cent /kWh	5.7	Standard tax rate

[1] EnerTax = energy tax; EnvirTax = environmental tax; [2] LPG = liquid petrol gas;
[3] NG = natural gas; [4] RME = rape oil methyl ester; [5] EL = quality "EL"; [6] S = sulphur

The results available show that in the long term hydrogen is the most promising fuel with respect to raw material availability and CO_2 reduction. In the short and medium term, natural gas can be recommended for passenger cars with internal combustion engines because of the attractive cost structures and high availability. Methanol was ranked between these two fuels; in the case of commercial vehicles, methanol was in first place, ahead of natural gas; natural gas is not suitable for motor vehicles with fuel cells (PEFC) and an electric motor. – Filling stations and vehicles are being tested in the so-called "Clean Energy Partnership" (CEP).

2.2 Summary of Chapter 2

In the long term, hydrogen is the most promising fuel with respect to raw material availability and CO_2 reduction. In the short and medium term, natural gas can be recommended. Methanol was ranked between these two fuels.

3 Methanol and alternative fuels for road traffic

Methanol and GTL (gas-to-liquid) fuels are based on synthesis gases, which are primarily produced today from natural gas (**Figure 3**), but also from other feedstocks. A survey of different GTL processes can be found in [GTL 2003]. Methanol can be further processed to dimethyl ether (DME) or olefins.

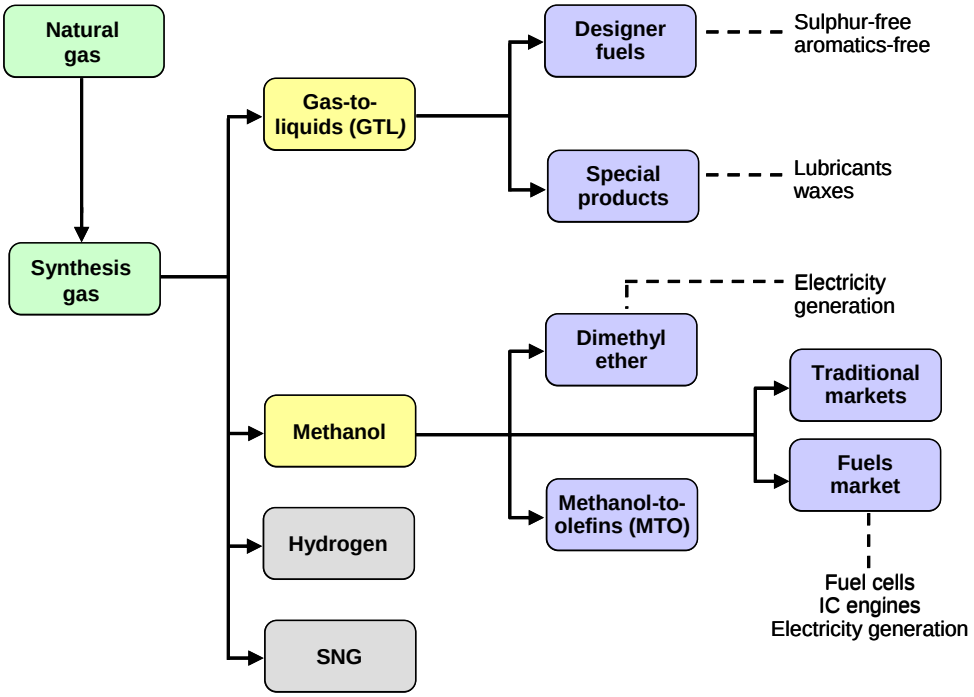


Figure 3: Pathways of using synthesis gas from natural gas (after [METHANEX 2003])

Methanol is primarily (80%) produced today by steam reforming of natural gas and subsequent catalytic synthesis in large plants and used in the chemicals sector; this requires a high degree of purity (AA grade); on the other hand, the quality requirements for use as a fuel in the transport sector are not yet defined (fuel grade). The methanol production capacity worldwide is about 35 million t/y (2003); it may exceed 40 million t/y after 2005 [MFCA 2003]. Consumption is currently in the range of 30 million t/y, about one third being apportionable to the USA [McCASKILL 2002]. Europe has a production capacity of 4 million t/y with a capacity utilization

of 3 million t/y in 1999 [VRIENS 2000]. The use of methanol is largely focused on the chemicals market today (about one third for formaldehyde worldwide – in Europe about 50% of the methanol market; also for acetic acid, methanol derivatives and solvents) [McCASKILL 2000], [McCASKILL 2002].

Methanol has been used as a fuel for:

– internal combustion engines, in California/USA: M85 (passenger car) with filling stations (without significance today),
– the M100 programme (M85) in Germany 15–20 years ago; 100 cars and a few filling stations, inter alia at UK Wesseling/DEA (without significance today),
– the M100 DI (direct-injection) engines in the USA and Germany (diesel concept with ignition aid), at FEV/Aachen, Volkswagen and EPA/USA (without significance today),
– fuel cell power trains with low-temperature fuel cells (without significance today).

Apart from its direct use as a fuel for vehicles, methanol is also being used as feedstock for the production of methyl tert-buthyl ether (MTBE). As a blend component for gasoline MTBE works as an octane booster with simultaneous oxygen enrichment (cf. **Chapter 11.2**).

Methanol (CH_3OH) is also used for the production of dimethyl ether (DME, C_2H_6O). DME can be used as a diesel substitute fuel in diesel combustion engines without particulate emissions. DME is produced from methanol splitting off water and it is gaseous at ambient temperature and pressure and is stored and transported in the liquid state at low pressures (DME: LHV=28 MJ/kg; methanol: LHV=20 MJ/kg).

	2 CH_3OH	**=**	**C_2H_6O**	**+**	**H_2O**
Molar mass / (kg/kmol)	2 x 32	=	46	+	18
Molar mass / (%)	100	=	72	+	28

Methanol is also used for the transesterification of vegetable oil. The physical properties of the oil can be modified by changing the molecular structure of the fatty acid molecules. This chemical process – so-called transesterification – is used to fulfil the engine-specific requirements of a fuel. Transesterification or alcoholysis is understood to be the exchange of an alcohol (e.g. trivalent alcohol, glycerol) bound in ester (here vegetable oil) for another one (e.g. monovalent alcohol, methanol). Feedstocks are rape oil and methanol (about 5% relative to RME in terms of energy). The

end products are rape oil methyl ester (RME) (RME: LHV=37 MJ/kg; diesel fuel: LHV=43 MJ/kg) and glycerol.

Associated gas according to [LIEBNER 2002] is available in large quantities worldwide with about 10^{11} m^3/a (corresponding to 130 million t/y of methanol in terms of energy) at low cost [HOLMES 2000], [HOLTMANN 2001]. At a cost level of $\leq$ 1 \$/$GJ_{associated\ gas}$, methanol production plants with capacities of 5,000 t/d of methanol (so-called megaplants) can be constructed. This would possibly lead to a declining utilization of already existing global production capacities, even by dual use of reserves [3], but would above all significantly influence the production costs for methanol. Single-stranded megaplants according to the process of combined reforming with multi-stage methanol synthesis [STREB GÖHNA 2000] are being constructed inter alia in Trinidad and Bandar Assaluyeh/Iran according to the LURGI process [LURGI 2000] and [JONES 2000] (cf. **Chapter 7**). Smaller plants – as in Germany – often have the advantage of short delivery channels to the consumer, but the proceeds for the methanol produced will be lower due to the higher generating costs.

In the case of large gas volumes available far away from the consumers (remote gas, stranded gas), a suitable strategy for their use has to be found. According to [HOLTMANN 2001], the transport of electric current (which is produced in situ "at the well" with the aid of natural gas) via long-distance lines or the transport of natural gas in pipelines is only economically efficient up to distances of 2,500 km. In contrast, the in-situ production of LNG (liquefied natural gas), DME (dimethyl ether), hydrogen, methanol or a combined production of methanol and propylene or methanol and ammonia would represent an alternative solution for use. Before realizing such options, however, it is necessary – as a function of natural gas qualities (content of sulphur, carbon dioxide, nitrogen and higher hydrocarbons) – to analyse the markets and the total primary energy input while minimizing CO_2 emissions.

[3] Associated gas has so far usually been vented or flared. This gas could be used to produce and utilize methanol. The corresponding amount of fossil-based fuel in terms of energy would then be saved and the associated CO_2 emissions avoided. Dual use of reserves would then mean: using the associated gas and saving fossil-based fuel.

3.1 Methanol for MTBE production

A considerable proportion of methanol is used for the production of MTBE. In Europe and the USA, MTBE is hitherto used as gasoline blend in the transport sector; it serves as an octane booster and a “clean” oxygen-enriching component in carburettor fuel. The aim is also a reduction of CO emissions according to the environmental regulations in the USA, the EU and other countries. Unlike Europe, however, the USA is clearly changing its attitude to the use of MTBE.

MTBE ($C_5H_{12}O$) is produced from methanol and isobutene (C_4H_8). The mass-related lower heating value of MTBE (LHV=35 MJ/kg) is almost twice as high as that of methanol (LHV=20 MJ/kg) (**Table 38**).

	$CH_3OH + C_4H_8$	=	$C_5H_{12}O$
Molar mass / (kg/kmol)	32 + 56	=	88
Molar mass / (%)	36,4 + 63,6	=	100

Isobutene is produced during naphtha steam reforming, from cracked gases of the oil industry, and during the catalytic dehydrogenation of butane or isobutane. In recent years, the extensive use of MTBE has governed the demand for methanol worldwide. In view of the hazards to drinking water due to leakages from gasoline tanks in California [FISLER 2000], a discussion has developed in the USA on the permissibility of the use of MTBE as a lead substitute and an oxygen-donating fuel component (a detailed survey of the environmental behaviour (Henry coefficient) and the microbial degradation and dangers to health of MTBE is given in [LINNEMANN 2003]). The ban on the use of MTBE in California has become effective by the end of 2003 (cf. **Chapter 11.2**). If the second largest sales market for methanol were to shrink for this reason, considerable surplus amounts of methanol could exert pressure on the market.

3.2 M85 for direct-injection combustion engines

As long ago as the early eighties, engines were developed that could run on methanol-gasoline fuel mixtures. These fuels initially only contained 15% methanol (M15), but the methanol fraction was later gradually increased. Additional solubilizers are required under certain conditions and depending on the water content of the methanol. Up to a methanol fraction of approx. 3% no modifications to the vehicle (engine and peripher-

als) are needed. Admixing 3%-15% methanol requires an adaptation of the materials of the fuel system (plastics) that directly come into contact with methanol.

Pure methanol was originally not suitable for use in vehicles, since its low vapour pressure led to cold-start problems. For this reason, 10–15vol% of a gasoline fraction was added to the methanol. In order to optimally utilize the fuel properties of M85, modifications to the existing engine concepts were necessary.

Initial experience with M85/M90 was made with modified gasoline engines, in which the high octane numbers enabled an increase of the compression ratio compared to gasoline operation. Due to the wide ignition range of methanol it was additionally possible to realize lean operation. As early as 1982 it was possible to achieve more favourable consumption values for methanol vehicles in the ECE cycle than for comparable gasoline vehicles. Due to the lean operation, low flame temperature and high evaporation heat of methanol fuels, the methanol vehicles also displayed extremely low nitrogen oxide emission values. In the following years, the engine concept was further improved by adapting the combustion chamber configuration and the carburetion system to the increased compression values.

Optimized concepts for M85 were tested worldwide and developed almost up to the production stage. Due to the lack of a large-area supply infrastructure, development has been increasingly focused on more universal flexible fuel vehicles (FFV), which can run on M85, gasoline and arbitrary fuel mixtures. This ensures full user mobility. VOLKSWAGEN developed the multi-fuel-concept vehicle (MFC/MFV) in the late eighties and from 1990 took part in a major test programme with about 100 vehicles in California [WEGENER 1999].

The rising demands made on the quality of exhaust emissions led to the development of an engine concept for operation with pure methanol (M100). In 1990, the companies FEV/Aachen, Volkswagen and EPA/USA presented a concept for a methanol engine with direct injection (DI) based on a standard 1.9 l DI diesel engine of Volkswagen. Test operation showed very low NOx and particulate emissions in comparison to the diesel engine. The emissions of non-methane organic gases (NMOGs) were clearly higher than from comparable diesel engines. The NMOGs largely consisted of unburned methanol (with low ozone forming potential) from the cold-start phase (whereas unburned hydrocarbons from the cold-start phase of gasoline/diesel engines have a high ozone forming potential). In contrast

to the gasoline engine, the DI methanol engine displayed very low aldehyde emissions.

This engine concept combines the advantage of the high efficiency of direct-injection, high-compression engines with that of the particulate-free combustion of alcohols. Due to the low cetane number of alcohol fuels, a spark ignition system or an additional injection of diesel fuel is required. The glow ignition system leads to satisfactory cold-start and cold-shutdown behaviour. A great problem, however, is the increased susceptibility to corrosion and wear due to the poor lubricating effect of methanol [WEGENER 1999], [HILGER et al. 1990].

In California and some cities in the USA, flexible fuel vehicles with internal combustion engines running on gasoline or methanol/fuel mixtures were in operation. The vehicles were only equipped with one tank, but had a fuel sensor. Approx. 15,000 passenger cars of about 20,000 were run in California. This project involved the companies Ford, GM, Chrysler, VW, Nissan, Toyota and Mercedes. With the participation of ARCO, Chevron, Exxon, Mobil, Shell, Texaco and Ultramar, 330 methanol transit buses with Detroit diesel 6V92 engines were in operation in California, whereas less than 100 filling stations were available for refuelling with M85. Certified vehicles are no longer on the market today; the 10-year programme with M85 was terminated, the last filling stations are being closed down or modified. Within the framework of the California Fuel Cell Partnership, there has been a methanol filling station of Methanex in Sacramento/CA since 25.4.2002. Methanol does not play a role in the Californian near-term clean fuel infrastructure and vehicles planning [LYNN 2001], [WARD 2002], [CEC 2001], [MI 2003].

3.3 Methanol for fuel cells with reformers

Novel power trains for traffic will only be able to attain a great application potential if they contribute towards conserving existing energy resources and reducing pollutant emissions due to higher system efficiency than internal combustion engine drives. However, they must also be comparable to conventional vehicles with respect to performance, usefulness (useful interior and payload) and range. And ultimately the costs must be competitive.

To this end, the overall efficiency and total emissions of full fuel cycles (energy balance from primary energy carrier up to the vehicle in operation, cf. **Table 5**) must be improved in comparison to conventional drives

for traffic. Reductions in weight, recovery of braking energy or traffic guidance systems can provide further contributions. The use of low-carbon primary energy carriers in drive systems with optimum energy management also contributes to emissions reduction. Internal combustion engine drives based on the fossil primary energy carrier oil are dominant today.

Electric drives with batteries as the power source currently only represent a niche market. The infrastructure of mobile energy supply is also characterized by internal combustion engine drives. Modern industrial nations have filling stations all over the country.

Among all the energy converters and storage systems suitable for vehicles, the electrochemical systems in combination with electric motors have a higher efficiency than the internal combustion engines available. Such electric drives can provide a significant contribution towards solving the problems of mobile energy supply. In using a fuel cell as the energy converter in a vehicle, the converter and storage tank are arranged separately as in the case of conventional drives; power and energy reserve (and thus range) can be selected independently of each other.

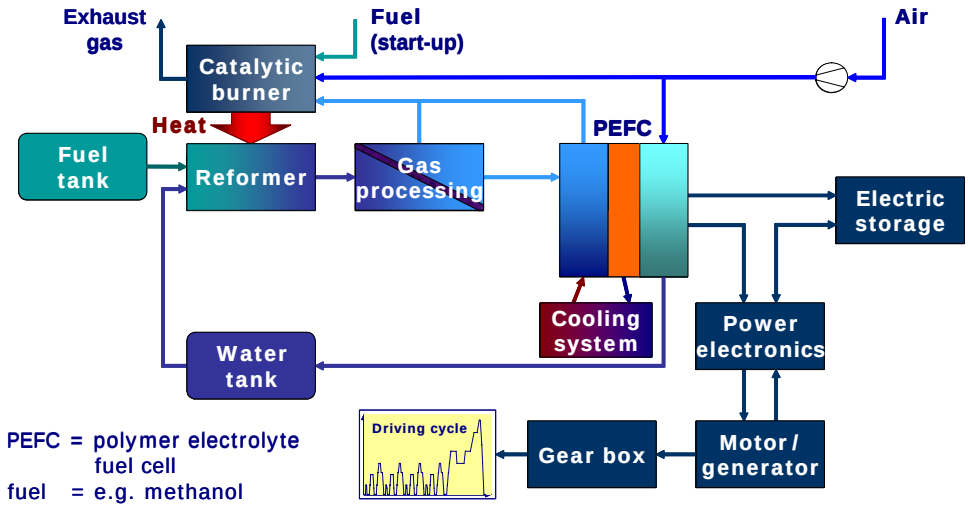


Figure 4: Fuel cell power train with on-board hydrogen production from methanol

Since fuel cells for use in mobile applications (low-temperature fuel cells with polymer membrane as the electrolyte – polymer electrolyte fuel cells, PEFCs) need hydrogen and air as educts according to the present state of development, hydrogen would have to be available at the filling station as

the energy carrier for direct use (hydrogen variant) and methanol or liquid hydrocarbons (such as gasoline or diesel) for indirect use. The indirect use of reformed methanol (**Figure 4**) or liquid hydrocarbon (both with on-board production of hydrogen) reduces the efficiency of the fuel cell power train in comparison to direct use. There is at present no infrastructure for refuelling methanol-operated fuel cell vehicles.

In a drive system for mobile application with methanol tank and reformer, fuel cell, energy storage and electric motor (**Figure 4**), a liquid methanol/water mixture is used as the fuel, which under ambient conditions exhibits physical properties similar to those of conventional fuels. Water does not have to be additionally filled in but is obtained as the oxidation product of hydrogen, condensed out of the off-gas mixture of the fuel cell and passed into the tank. The methanol/water mixture is delivered by a fuel pump into an evaporator, where it is heated, evaporated and superheated. The superheated methanol/water mixture is then converted into a hydrogen-rich synthesis gas in a reformer. Heat for the heterogeneously catalysed reaction is supplied by a low-emission catalytic burner, in which the residual gases are converted into energy.

If in today's large-area traffic the fuel cell power train of a passenger car were to be operated with hydrogen and air from a filling station (hydrogen/air variant), this would pose considerable problems: the storage density of present-day hydrogen storage tanks is too low (leading to weight and volume problems) and an infrastructure for hydrogen supply does not exist for these cars. The costs before tax for hydrogen based on natural gas would be 2–3 times higher than for gasoline or diesel fuel even in the case of a high substitution rate of about 50%. However, the evaluation of these elevated costs is relativized by the fact that – in comparison to gasoline-fuelled vehicles with internal combustion engines – the hydrogen-fuelled vehicle has an about 40% lower energy demand (cf. **Table 3**, **Table 4**). **Figure 2** shows today's specific energy carrier costs (before taxes) for fuel supply in Germany as a function of the specific CO_2 emissions which arise in delivering the respective fuel up to the filling station and using 1 MJ of the respective energy carrier.

In the medium term, a simpler solution approach could be to tank up cars with liquid energy carriers such as methanol and gasoline/diesel and produce a hydrogen-rich synthesis gas from these on board the vehicle. Problems such as range and infrastructure can thus be solved more easily than for the hydrogen variant, but on-board hydrogen production impairs the dynamics of the power train and requires the installation of an additional

short-term storage system for acceleration phases. The use of methanol or gasoline/diesel gives rise to the question of whether the fuel cell should be modified with the aim of oxidizing hydrogen-rich synthesis gases also containing CO, CO_2 and water in the fuel cell using atmospheric oxygen. Finally, the higher system complexity requires extra costs.

In research and development, at present, the methanol and gasoline/diesel variants are only being dealt with to a limited extent as transition solutions on the road to the use of pure hydrogen. In the medium to long term, the development of the fuel cell for direct methanol use, the direct methanol fuel cell, DMFC, is also being pursued [JÖRISSEN 2000]; in the long term, providing a low-cost infrastructure, if possible, based on hydrogen produced from renewable sources, the use of the above-mentioned hydrogen variant is envisaged, which is currently implemented in most of the fuel cell concept cars.

In contrast to mobile applications, the DMFC has a high potential for use in portable applications for electric power generators with fuel cells [HFC 2003] (cf. **Chapter 11.1**) or as power sources for small traction applications in industry such as floor conveyors. Relevant studies are being conducted worldwide, inter alia at Research Centre Jülich [DOHLE 2003].

The development of fuel-cell-powered vehicles into products for a possible mass market is influenced by many factors. A comparison of the balances of the energy and emission chains for fuel supply and passenger car operation (well-to-wheels analysis) in Germany shows according to [KRAKE 2005] in part advantages of the cars with fuel cells over those with other drive systems (**Table 5**). This includes advantages concerning:

– primary energy requirements (about 25% lower for future C.H_2-FC passenger cars compared to gasoline-ICE cars, but no bonus for CH_3OH-FC cars with CH_3OH production from natural gas in Germany),
– CO_2 emissions (about 38% lower for future C.H_2-FC passenger cars, about 13% lower for methanol-FC cars with methanol production from natural gas at the well, both in comparison to gasoline-ICE cars) and
– regulated emissions (H_2-FC cars are zero-emission vehicles; methanol-FC cars are clearly below the EURO-4 standard and fulfil the stricter standards of Californian ZEV legislation.

Moreover, fuel cell vehicles must be comparable to modern vehicles with gasoline/diesel drives concerning performance and driving comfort, payload, range and cost. Additional advantages and new value-adding potentials must be perceivable for fuel cell vehicles.

A balance comparison of the full fuel cycles is only possible to a limited extent due to the different development level of fuel cell power trains. Thus, the development of fuel cell power trains with on-board reforming of conventional diesel from crude oil or Fischer-Tropsch diesel from natural gas (FT-d) and direct methanol supply to the fuel cell (DMFC) is much less advanced than that of indirect methanol use (on-board reforming) or direct hydrogen use (PEFC). A future gasoline drive was chosen here as the basis for comparison (column 2 in **Table 5**).

In comparison to German or European studies on gasoline-fuelled reference vehicles of today, American balances (such as [MFCA 2003] for fuel cell vehicles display greater reductions in primary energy requirements and CO_2 emissions than should result for a balance based on a future reference vehicle. This is due to the fact that the reference vehicle in the American balances is a gasoline-fuelled passenger car of today with a drive efficiency of 13–17%, which depending on the vehicle corresponds to a fuel consumption of about 7–8 l gasoline/100 km. A car drive of the future, however, according to [GRUBE et al. 2001] will be able to reach a drive efficiency of about 22% and will consume about 5 l gasoline/100 km (for this estimate, the weight and the vehicle parameters of the above reference vehicle and driving through the European driving cycle were assumed; cf. **Figure 4**). This reduces the reductions in primary energy demand and CO_2 emissions.

The results of a comparison of different fuel/vehicle systems with respect to primary energy input and climate-relevant emissions are shown in **Table 5** [KRAKE 2005]. The reference vehicle chosen was a gasoline car, which relative to diesel cars exhibits a higher energy demand in the driving cycle, but has lower exhaust gas emissions from the present perspective (no particulate emissions). For the associated fuel supply, primary energy expenditure on exploration/extraction at the well, long-distance transport as well as refining (regional refineries in Germany) and distribution by truck have been included. Other full fuel cycles have very different supply structures depending on their origin and on the physical properties of the primary and secondary energy carriers as well as on the choice of the site for fuel production (remote, regional and local). In the literature, in part very different boundary conditions are assumed, which only allow a limited comparability of the results.

Table 5: Energy, efficiency and CO_2 balances of full fuel cycles for compact passenger cars [KRAKE 2005]

PES **FES** **FES plant**	**Crd.oil** **gasoline** **reg**	**Crd.oil** **diesel** **reg**	**NG** **FT-d** **rem**	**NG** **C.NG** **local**	**NG** **C.H_2** **rem / reg**	**EL** **C.H_2** **local**	**NG** **CH_3OH** **rem**	**NG** **CH_3OH** **rem**	**NG** **L.H_2** **rem**
EC / engine	ICE	ICE	ICE	ICE	FC EM	FC EM	ref+ FC EM	DMFC EM	FC EM
m_{car} [kg]	1,064	1,062	1,062	1,064	1,164	1,164	1,257	1,161	1,076
η_{FSC} [%]	81	85	61	81	64/63	25	64	64	51
E_{car} [MJ/100km]	153	132	132	145	91	91	125	111	87
η_{car} [%]	22	25	25	23	39	39	30	31	39
E_{FFC} [MJ/100km]	190	155	215	180	142/145	362	195	173	170
η_{FFC} [%]	18	21	16	19	25/25	10	19	20	20
$CO_{2,\ FFC}$ [kg/100km]	13.7	11.3	14.3	10.6	8.4/8.5	21.2	11.9	10.6	9.7

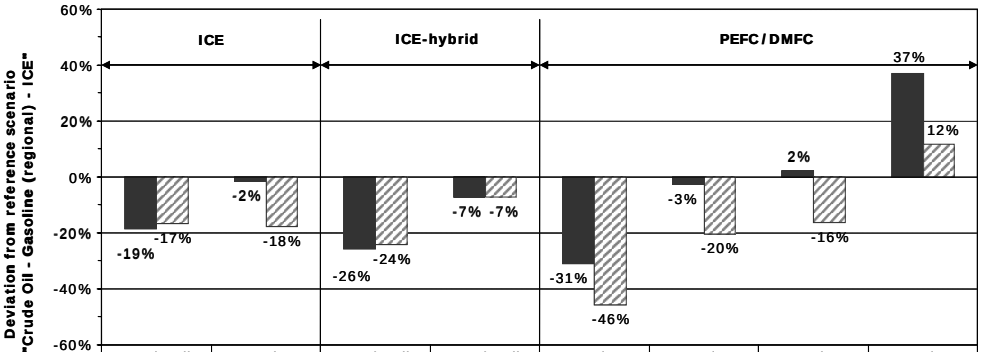
Row 1: ES = energy source; PES = primary ES; FES = final ES; FES plant = plant for the conversion of PES into FES (sites: loc=local, reg=regional, rem=remote); Crd.oil = crude oil; NG = natural gas; EL = electricity mix Germany (for water electrolysis); FT-d = Fischer-Tropsch diesel; C.NG = compressed NG; C.H_2 = compressed H_2; CH_3OH = methanol; L.H_2 = liquefied H_2. – **Row 2**: EC = energy converter; ICE = internal combustion engine; FC = fuel cell (PEFC); ref+FC = reformer with FC; DMFC = direct methanol FC; EM = electric motor. – **Row 3**: car = passenger car. – **Row 4**: FSC = fuel supply chain (PES up to FES). – **Row 5**: E = energy demand. – **Row 6**: η = efficiency. – **Row 7**: FFC = full fuel cycle (PES up to wheels) .

In order to enable a better evaluation of the balancing presented here, mean values from the comparison of international studies were used for the criteria “primary energy input” and “climate-relevant emissions”, as can also be seen in **Table 5** [KRAKE 2005] (FFC). For calculating the integral well-to-wheels value (MJ_{PE}/km), the mean value of the study data on well-to-tank fuel supply (MJ_{PE}/MJ_{fuel}) was multiplied by the tank-to-wheel value for the vehicles (MJ_{fuel}/km). The potentials for improvement compared to the reference scenario, which can be derived from these mean values, are shown in **Figure 5**.

It can be seen that except for the use of Fischer-Tropsch diesel (based on natural gas) in fuel cell power trains all the fuel/vehicle systems investigated display advantages over the reference system concerning the balance of greenhouse gases.

A comparison of internal-combustion-engine-based vehicles including the hybrid variant with the fuel cell vehicles shows that under the chosen

boundary conditions the highest reduction of primary energy input and greenhouse gas emissions is attainable by the direct use of hydrogen (compressed hydrogen $C.H_2$ from natural gas) in fuel cells.



	Crude Oil Diesel (regional) ICE	Natural Gas C.NG (on-site) ICE	Crude Oil Diesel (regional) ICE-hybrid	Crude Oil Gasoline (regional) ICE-hybrid	Natural Gas C.H2 (remote) PEFC	Natural Gas MeOH (regional) PEFC	Natural Gas MeOH (regional) DMFC	Natural Gas GTL (remote) PEFC
PEC	-19%	-2%	-26%	-7%	-31%	-3%	2%	37%
GHG	-17%	-18%	-24%	-7%	-46%	-20%	-16%	12%

PEC=primary energy carrier; GHG=greenhouse gas; reference system is the gasoline-fuelled vehicle with ICE (oil-gasoline (regional) ICE); data calculated from mean values of [ADL 2002], [ECO 2001], [FVV 1998], [GM 2002], [GOSSEN GRAHL 1999], [GREET 2002], [IEA 1999], [KRAKE 2005], [MIT 2000], [PEHNT 2001], [CONCAWE 2005]

Figure 5: Reduction potential of future vehicle/fuel systems (passenger car) in relation to primary energy input and climate-relevant emissions; after [GRUBE et al. 2003]

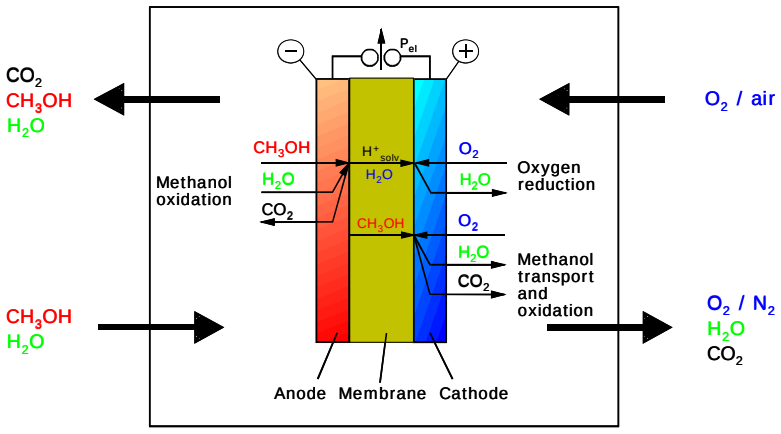
3.4 Methanol for fuel cells without reformers (DMFC) [4]

Direct methanol fuel cells (DMFCs) directly convert the liquid fuel methanol into electric current. In comparison to fuel cell systems operated with pure hydrogen or hydrogen-rich gases from reforming processes, fuel supply is effected directly via liquid methanol. In addition to the very high energy density of methanol, the DMFC is characterized by easy handling and unproblematic refuelling. It may be used in different power classes. For portable applications in the very small power range, entry into the market is expected within the next few years.

[4] Chapter 3.4 sources: figures after Mergel/Dohle (FZJ), 2005.

3.4.1 Fuel for direct fuel cells

Liquid fuels have the advantage of a higher storage density compared to gaseous fuels. This is particularly effective in the system whenever long operating times are to be achieved with one fill-up, which is an advantage over batteries. For most fuels – with the exception of hydrogen – a chemical intermediate step is required to make the fuel usable for the fuel cell: it is converted into hydrogen by reforming and additionally purified. On the other hand, a system becomes much simpler if hydrogen can be directly converted, i.e. the reforming step is circumvented. This is especially the case for low-temperature fuel cells. Direct fuel cells, which are capable of directly converting a carbon-containing molecule at the electrode, suggest themselves as an alternative here. Circumventing the reforming step has to be paid for with higher overvoltages, electrochemical losses, at the electrodes.



Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$

Cathode: $1.5\,O_2 + 6\,H^+ + 6\,e^- \rightarrow 3\,H_2O$

Cell: $CH_3OH + 1.5\,O_2 \rightarrow CO_2 + 2H_2O$

Figure 6: Principle of the DMFC

An often cited disadvantage of methanol is its toxicity. It is forgotten here, however, that methanol is much less toxic than the established gasoline, which due to its benzene content is, moreover, also carcinogenic and teratogenic (cf. **Chapter 8, Table 30**). Methanol, in contrast, although being acutely toxic, is neither teratogenic nor carcinogenic and, moreover, much more easily biodegradable than gasoline or diesel. It should be borne in

mind when handling methanol that due to its water solubility it can penetrate through the skin into the body, but this can be prevented by protective measures. Handling methanol is therefore unproblematic in the professional area where the personnel can be adequately instructed and proceeds with sufficient care. In the hobby and household sector, adequate passive safety measures such as hermetically sealed receptacles permitting safe handling would be a precondition for use. In any case, however, it must be stated that methanol is much less dangerous than gasoline which we are used to handle today.

3.4.2 Principle of the DMFC

The central component of the DMFC is the membrane electrode assembly (MEA). The membrane – a proton-conducting plastic foil – separates a methanol/water mixture on the anode side of the fuel cell from the air on the cathode side. In detail, the catalytically activated partial reactions shown in **Figure 6** take place.

Inside the cell, the methanol is not pure on the anode side, but for reasons of stoichiometry must be present with water in a ratio of at least 1:1. Since the membrane is permeable for methanol, a higher dilution of the methanol is required in real operation. In order to keep the losses due to methanol permeation low, the lowest possible methanol concentration is therefore aimed at on the anode side.

The anode side is normally run in a loop, in which the methanol/water mixture is continuously recycled. The gaseous carbon dioxide produced during the anode reaction is discharged. The recycling configuration also serves to transport the heat losses from the stack and dissipate them to the environment, for example, via a heat exchanger. Methanol is continuously fed into the loop to compensate for the methanol consumption.

The electrochemical reactions in a DMFC (**Figure 6**) proceed much more slowly than in a hydrogen/air fuel cell. The reaction velocity can be influenced above all by the design and structure of the MEA.

In order to realize a DMFC system, high-performance electrodes are therefore required, which ensure rapid electrochemical reaction processes [HAMNETT 2003]. The electrodes essentially consist of a conductive graphite fabric, which is in electronically conducting contact with the catalyst layer. Binary Pt/Ru catalysts are normally used on the anode and pure Pt on the cathode. Ionically conductive fractions are added to the catalyst

layers, which are normally introduced as a finely distributed membrane material during electrode fabrication.

The currently most commonly used membrane material is the perfluorinated sulphonic acid polymer Nafion from DuPont. However, it has some major disadvantages, especially in DMCF operation, so that alternative materials are intensively explored which do not exhibit these disadvantages or only to a minor extent.

The proton conductivity of Nafion is only given if the membrane is saturated with water. In methanol operation, humidification is always given due to the liquid, aqueous fuel. Since methanol is soluble in water, however, the membrane in addition to water also takes up methanol, which is then passed to the cathode through the membrane. This leads to fuel loss and a degradation in performance due to mixed-potential formation and catalyst poisoning at the cathode.

Thus, for example, the following difficulties are encountered in the practical operation of a direct methanol fuel cell:

- potential losses at the anode due to low catalyst activity,
- losses in efficiency due to fuel losses caused by methanol permeation through the electrolyte membrane,
- potential losses at the cathode due to mixed-potential formation.

3.4.3 Development areas

Market entry for DMFCs is currently seen in the area of portable power supply for laptops, mobile phones, PDAs and for mobile electricity supply up to 5 kW.

In order to introduce such systems onto the market, they must be lightweight and compact. Therefore, high power densities are already needed at moderate operating temperatures between 10 and 50 °C. A basic requirement for market entry, apart from some niche applications, is, however, to achieve a cost level that is comparable to existing technologies. **Table 6** shows some performance targets for different power classes and application fields of portable fuel cell systems for possible market entry [DOE 2002].

Thus, present-day DMFC systems with about 140 Wh/kg are still two to three times as heavy as comparable lithium/ion batteries. The fuel cell stacks together with pumps, fans and electronic controls as well as the methanol tank require so much space that a module e.g. for a laptop is by far not conceivable.

Table 6: Performance targets for fuel cell systems (after [DOE 2002])

Performance targets	Power range and application		
	≤ 20 W Mobile phone, PDA [1]	**20–50 W** Laptop computer [2] [3]	**1–5 kW** Auxiliary power units, small mobile appl. [2] [3]
Specific power [4]	100 W/kg	n.d. [5]	200 W/kg
Power density	100 W/l	n.d. [5]	200 W/l
Specific energy [4]	n.d. [5]	600 Wh/kg	n.d. [5]
Energy density	1,000 Wh/l	n.d. [5]	n.d. [5]
Efficiency [6]	n.d. [5]	25% com. [7] 50% mil. [7]	30%
Costs	3 $/W	400 $ (20 W system) 1,000 $ (50 W system)	1 $/W com. [7] 3 $/W mil./ind. [7]
Service life	5,000 h	1,000 h (~ 2 a @1.5 h/d)	1,500–2,000 h com. [7] 5,000 h mil./ind. [7]

[1] Target 2010; [2] Target 2007; [3] Operating temperature 10–50 °C; [4] Mass-specific; [5] No data available; [6] Electrical power output (FC system) / input power (fuel consumed, HHV !); [7] Application: ind.=industrial; com.=commercial; mil.=military

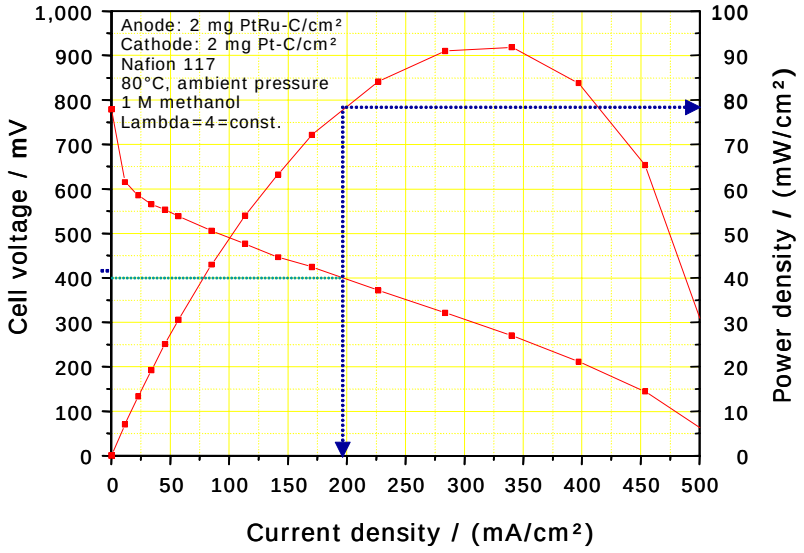


Figure 7: Cell voltage and power density of a DMFC at 80°C [Source: Mergel/Dohle FZJ]

In the range of high electric mass-specific power and power density, above all membrane electrode assemblies must be developed that work with much higher area-specific power than the 50 mW/cm² which is normal today at moderate operating temperatures around 50 °C [DILLON et al. 2003]. The performance target is about 100 mW/cm² here to compete with lithium/ion batteries. Today, MEAs reach these power densities only between 70 and 80 °C at catalyst loadings of 4 mg/cm^2 and cell (**Figure 7**). Furthermore, the costs must be lowered by reducing the catalyst loading to below 2 mg/cm² per single cell. A price that is comparable to storage batteries can only be achieved by increasing the area-specific power while minimizing the noble metal requirement.

Portable fuel cells, moreover, will only have a chance of market entry if questions concerning the infrastructure, standards and regulatory requirements are clarified.

The following research and development needs for the DMFC can therefore be derived from the requirements to be fulfilled:

– optimisation of the electrocatalysts for methanol oxidation,
– improvement of the electrode structure,
– development of novel membrane materials with reduced methanol permeation,
– development of methanol-insensitive oxygen catalysts for reducing mixed-potential formation,
– system simplification and system integration.

3.4.3.1 Electrode structure

The microstructure of the electrodes is essential for their performance efficiency and for optimum utilization of the catalysts in the fuel cell. In contrast to hydrogen- or reformate-supplied polymer electrolyte fuel cells (PEFCs), the anode side is supplied with methanol-containing solution. This requires basically different structures in the diffusion layer and electrode. Whereas the PEFC has problems with membrane exsiccation and thus increased resistances, an excessively high fraction of water is to be observed on the cathode side of the DMFC in most cases. Research and development goals are therefore structures adapted to these changed water management requirements. In the DMFC, the differences in water content across a cell's cross-section are much more inhomogeneous than in a PEFC. This requires better adapted or specially designed diffusion layers with hydrophobicity e.g. also inhomogeneously changed across the area.

Due to the reactions and the associated possible degradation of the catalyst, the active layer of the membrane electrode assembly (MEA) must also be optimized with respect to the given conditions. The German Aerospace Centre (DLR) has developed suitable aids, such as segmented cells, to locally determine the current density distribution in single cells and stacks and to perform local electrochemical impedance spectroscopy [WEISSHAAR et al. 2003]. This makes it possible to measure the influence of different operating parameters on MEA performance during operation and to develop adapted electrodes with inhomogeneous catalyst distribution.

3.4.3.2 New membrane materials

Various membranes are currently under development [GLUESEN/STOLTEN 2003]. Membranes on the basis of sulphonated aromatic polymers are currently being developed by several companies and research groups. They are regarded as fluorine-free alternatives to Nafion and are expected to be cheaper in mass production than Nafion. These polymers are mostly sulphonated in solution, and the membranes are produced in a casting process. The base polymers for this type of membranes are poly(etherketones), PEK, poly(etheretherketones), PEEK, poly(ethersulphones), poly(sulphones) and poly(imides). These polymers are very stable high-performance materials.

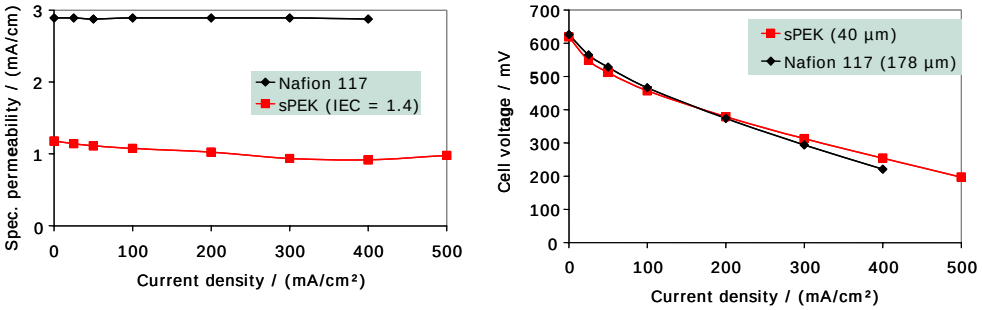


Figure 8: Specific methanol permeability and cell voltage of a sulphonated PEK (sPEK) membrane (80°C, 1 M methanol, 3 bar) [Source: Mergel/Dohle FZJ]

Many studies are based on PEK. The properties of the membranes depend on the quality of the base polymer, on the selectivity of the sulphonation reaction and on the membrane fabrication process. In comparison to Nafion, the sulphonated aromatic polymers take up slightly less water. Whereas Nafion has a few broad conductance channels, in which the sul-

phonic acid groups are in contact with water, these channels are narrower and more branched in sulphonated PEK. Therefore, a smaller drag coefficient may be expected, which was also experimentally confirmed [ISE/KREUER/MAIER 1999] causing lower methanol permeation (**Figure 8**). Today, this does not yet lead to lower performance losses in DMFC operation. Sulphonated aromatic poymers can, moreover, be modified by mixing with alkaline polymers forming a network [JÖRISSEN et al. 2002]. This can also increase the mechanical stability of the membrane and thus reduce swelling and methanol permeability.

3.4.3.3 Selective catalysts

The methanol that reaches the cathode due to permeation is partially oxidized on the platinum catalysts. This leads to mixed-potential formation at the cathode and thus to voltage losses during DMFC operation. In order to avoid these mixed potentials, methanol-insensitive catalysts with high activity are being developed to replace the platinum. After [HILGENDORFF et al. 2002] supported, selenium-modified ruthenium particles are

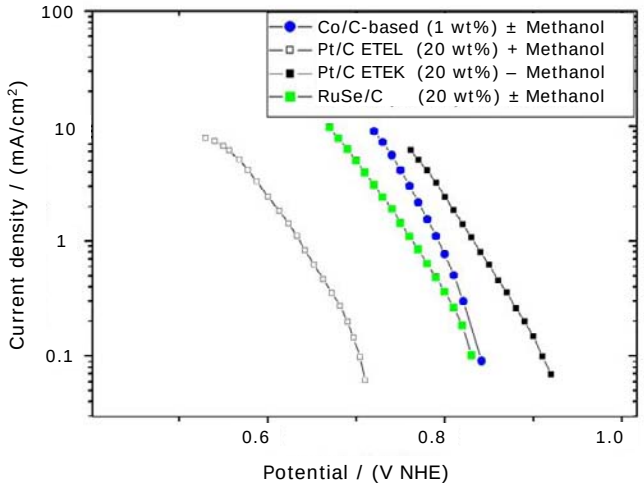


Figure 9: Oxygen reduction at the cathode: electrochemical activity of various catalyst materials (wt% of cathode material) in the presence (+) / absence (-) of methanol (Source: HMI)

particularly promising and materials in which atomic cobalt or iron centres are embedded in a highly porous carbon matrix. **Figure 9** shows the high electrochemical activity of various catalyst materials and the methanol resistance of the materials in comparison to platinum. Relative to the

metal content used, the cobalt-based catalysts even show a much better activity than commercial platinum catalysts, which is indicative of very active catalytic centres. On account of these properties, cobalt-based material is believed to have a high development potential. In addition, it is expected that the avoidance of expensive noble metals will lead to a cost advantage in fuel cell technology. Initial tests in DMFCs have shown, however, that the morphology of both the catalysts and the MEA still has to be optimized, before high power densities can be achieved.

3.4.4 Applications

Since the concept of direct methanol fuel cells for portable applications is attractive at present, important and impressive progress has been achieved in this technology by intensive development work worldwide.

In Germany, above all the activities of Smart Fuel Cell are known, who develop DMFC systems in the small power range and delivered the first small series of DMFC systems with a power of 25 W.

Due to the use of currently available membrane materials such as Nafion, the system for water and heat management must be of a much more complex design than that for a directly hydrogen-fuelled fuel cell. The first small mobile DMFC applications are therefore exclusively driven by hybrid systems [ADACHI 2003].

Research Centre Jülich equipped a commercial electric vehicle with a 1 kW DMFC system in 2004 [JANSSEN et al. 2004] (**Figure 10**), which in conjunction with a lithium/ion battery forms the hybrid drive of the vehicle. The fuel is pure methanol.

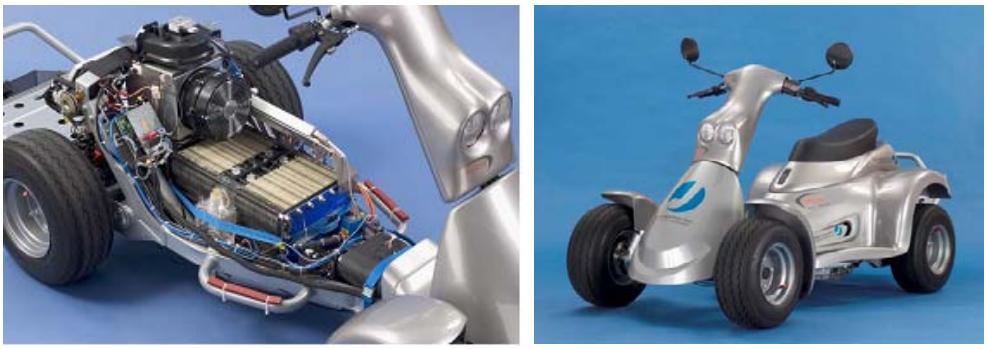


Figure 10: DMFC vehicle *JuMOVe* (Research Centre Jülich)

3.4.5 Outlook

Direct methanol fuel cells are attractive for various applications, above all, however, as battery or accumulator replacement, since DMFC systems permit longer operating times due to the high energy density of methanol. Important and impressive progress has been made concerning this technology due to intensive development work worldwide; however, the properties of the materials currently available on the market, especially those of the membranes, are not optimal for application in DMFC systems. Further research and development is indispensable in order to realize direct methanol fuel cells and DMFC systems with high efficiencies and power densities. The potential of this technology can only be fully exploited with new optimized materials.

3.5 Methanol for fuel cell powered passenger cars in the USA

Against the background of fuel cell development, several industrial companies founded the international Methanol Fuel Cell Alliance (MFCA). Its aim was to create the prerequisites for building up a market for fuel cells and methanol as the energy carrier. This included the advancement of topics such as fuel cell specification, consumer acceptance (health, safety, environment), government funding of demonstration projects, establishing the infrastructure and training programmes. The MFCA comprises the companies Ballard/CDN, BASF/D, BP/GB, DaimlerChrysler/D/USA, Methanex/USA, and Statoil/N [MFCA 2003]. In addition, the Methanol Specification Council of the methanol, vehicle and oil industries has been established, which currently has a report drawn up on the environmental, safety and health problems of methanol for fuel cell power trains in comparison to gasoline for internal combustion engines.

The California Fuel Cell Partnership (CaFCP) also supports the introduction of fuel cells in the motor vehicle market. CaFCP comprises fuel cell manufacturers (Ballard Power Systems, UTC Fuel Cells), automobile manufacturers (DaimlerChrysler, Ford Motor Company, General Motors, Honda, Hyundai, Nissan, Toyota, Volkswagen), power utilities (BP, Chevron, Texaco, ExxonMobil, Shell) and various American authorities. Concerning the fuel infrastructure, the associated members Air Products, Chemicals Inc. and Praxair are engaged in creating an infrastructure for hydrogen and Methanex one for methanol (a methanol filling station was opened in Sacramento on 24.4.2002). According to [CAFCP 2003], up to 70 passenger

cars and buses as well as various filling stations are currently being incorporated in a demonstration project. CaFCP already demonstrates the operation of hydrogen vehicles and plans to provide a “clean gasoline” as the third fuel (after hydrogen and methanol) and to demonstrate its application next year. “All car manufacturers in the CaFCP are in agreement that the first fuel cell vehicles that come onto the market will run on hydrogen from the filling station. Nevertheless, the members consider it important to further investigate all the fuels available” [LBSYS 2002].

3.6 Summary of Chapter 3

Vehicles with internal combustion engines for methanol (M85) are no longer commercially available. In Europe, no market is in sight for vehicles with internal combustion engines or fuel cells (with or without reformer), for which methanol would have to be additionally supplied as a fuel. Automobile manufacturers make no declarations of intent concerning the provision of passenger cars or commercial vehicles for fuel cell methanol operation (only DaimlerChrysler made the NECAR-5 passenger car available for a demonstration project within the framework of the California Fuel Cell Partnership, for which a methanol filling station was put into operation in Sacramento/CA in April 2002). No efforts at building up an infrastructure for methanol supply for road traffic are currently perceivable in the EU.

Direct methanol fuel cells (DMFCs) directly convert the liquid fuel methanol into electric current. In comparison to fuel cell systems operated with pure hydrogen or hydrogen-rich gases from reforming processes, fuel supply is effected directly via liquid methanol. DMFCs are attractive for various applications, above all, however, as battery or accumulator replacement, since DMFC systems permit longer operating times due to the high energy density of methanol. Important and impressive progress has been made concerning this technology due to intensive development work worldwide.

4 Methanol production

Methanol can be prepared in different ways. A method primarily used today is methanol synthesis following a synthesis gas production from natural gas. Instead of natural gas it is also possible, in principle, to use coal, residual oils, oil, cellulose or other waste masses (cf. [SVZ 2001] and **Table 7**). Synthesis gas production may have to be preceded by an extensive gas cleaning step, for example, if landfill gas is used; in these cases, methanol synthesis in small plants will not lead to economically efficient solutions.

Another way of methanol preparation is synthesis from CO_2 and H_2. However, this method only appears meaningful if, on the one hand, CO_2 is penalized and, on the other hand, hydrogen is produced from non-fossil sources. In this way, a "multiple use" of CO_2 is possible (**Figure 1**). CO_2 can be washed out from industrial gases; penalties and proceeds decide on the economic efficiency of the process.

Table 7: Methanol: feedstocks and potential use

Methanol	
Feedstocks	Potential use
Coal [1] Oil Natural gas Biomass [2] wood, sewage sludges, straw, miscanthus, etc. Waste materials Residual oils Landfill gas CO_2 + H_2 (renewable!)	Chemical raw material MTBE (octane *booster*) Gasoline *blend* M85/M90, VM [3] M100 DI ICE [3] M100 FC [4] H_2 production Gasoline production: MTG [5] Protein production [6]

[1] From climate aspects, CO_2 separation *(capture)* and sequestration are required; [2] Methanol (and diesel) from biomass [FREIBERG 2002]; [3] ICE = internal combustion engine; DI = direct injection; M85 passenger car in California and M100 programme in Germany and EPA/USA for ICE-DI diesel; [4] FC = fuel cell with electric motor in cars; methanol for on-board H_2 production for PEFC or for direct use in DMFC; [5] MTG = *methanol-to-gasoline* (LURGI process); [6] Bacterially produced proteins for cattle fodder; ICI process (in the 70s) did not prove economically efficient

A prerequisite for low-cost methanol production is large plants for methanol synthesis and the centralized availability of the corresponding primary energy carriers.

Another possibility of methanol preparation is the bacterially controlled fermentation of biomass, which, however, is not discussed here.

4.1 Methanol from natural gas

Most of the grade AA methanol for the chemicals market is produced worldwide today on the basis of natural gas involving the following transport and conversion steps:

– natural gas supply from the well to the methanol production plant,

– synthesis gas production by reforming,

– methanol production by synthesizing,

– methanol separation by distillation,

– storage, transport and distribution.

In each of these steps, energy must be supplied or extracted; in addition, emissions are released. Some specifications for methanol grades are compiled in **Table 8**.

Table 8: Various specifications for methanol after ([GSA 1998], [IMPCA 1999])

Characteristics	Grade A	Grade AA	IMPCA
Purity [1]/(wt%)	99.85	99.85	99.85
Sulphur [2]/(ppm)	–	–	0.5
Chlorides [2]/(ppm)	–	–	0.5
Acid [2]/(ppm)	30	30	30
Acetone [2]/(ppm)	30	20	–
Ethanol [2]/(ppm)	–	10	50
Water [2](ppm)	1,500	1,000	1,000
Non-volatile substances [2]/(mg/100 ml)	10	10	0.8
density (20°C) /(g/ml)	0.7928 [2]	0.7928 [2]	0.791–0.793

[1] minimum; [2] maximum

4.1.1 Synthesis gas production

The most expensive step in the production of methanol is the generation of synthesis gas (CO, CO_2 and H_2) from natural gas in the process step of reforming (cf. **Chapter 5 and Chapter 7.1.2**):

$$CH_4 + H_2O \Leftrightarrow CO + 3\,H_2 \qquad -\Delta H = -\ 205\ kJ/mol$$
$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad -\Delta H = \ \ 41\ kJ/mol \qquad \text{(eq. 4.1)}$$

According to the state of the art, two processes mainly come into consideration here: conventional natural gas reforming (endothermal, heterogeneously catalysed) with steam or carbon dioxide (CO_2 can be imported into the plant) and the combination of conventional reforming with autothermal reforming (heterogeneously catalysed), in which the addition of oxygen is needed for the partial oxidation of natural gas.

Conventional natural gas steam reforming with CO_2 addition at temperatures of up to 850 °C and pressures between 15 and 25 bars provides synthesis gases which are not optimally suited for methanol synthesis due to the hydrogen surplus; therefore, carbon dioxide may be added before or after reforming. In combined reforming, the synthesis gas optimal for methanol synthesis can be produced without the addition of CO_2 and in comparison to conventional reforming even with less investment and total energy expenditure.

In the synthesis gas production process with combined reforming (**Figure 11**), after desulphurization part of the process natural gas is reformed in the reforming unit heated with natural gas at a temperature of 800 °C and a pressure of about 34 bars. The gas is further reformed together with the remaining desulphurized natural gas in the autothermal reforming unit at 960 °C and 33 bars. The heat required for this purpose is made available by the partial combustion of the gas with oxygen. The residual methane content in the synthesis gas is lower and the apparatus expenditure less than in the case of conventional reforming.

4.1.2 Methanol synthesis

The synthesis gas is converted into methanol and water in a heterogeneously catalysed reaction system:

$$CO + 2H_2 \Leftrightarrow CH_3OH \qquad -\Delta H = \ 91\ kJ/mol$$
$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \qquad -\Delta H = \ 49\ kJ/mol \qquad \text{(eq. 4.2)}$$

The conversion of CO, CO_2 and H_2 into methanol and water is an exothermal process, which preferentially takes place at temperatures of 220–280 °C and a pressure of 40–110 bars with the catalysts available today; this conversion of CO and CO_2 into CH_3OH is characterized by the carbon conversion rate, which is defined as the ratio of the number of produced CH_3OH moles to the number of consumed moles (CO + CO_2). It rises with

rising system pressure, decreasing fraction of inert gases, rising CO/CO_2 ratio and dropping CH_3OH concentration at the end of the catalyst bed. A high carbon conversion rate is only achieved by recycling the process gas around the methanol reactor, extracting inert gas constituents and condensable products (methanol, water). Methanol synthesis can be realized with adiabatic reaction zones by feeding process gas between the zones or according to the isothermal process with a reaction tube cooling by saturated steam generation. The so-called crude methanol is extracted from the recycle loop as are the supplied inert gases; crude methanol is upgraded to grade AA methanol in two distillation columns, and the purge gas containing the inert gases is fed to the reformer for heating.

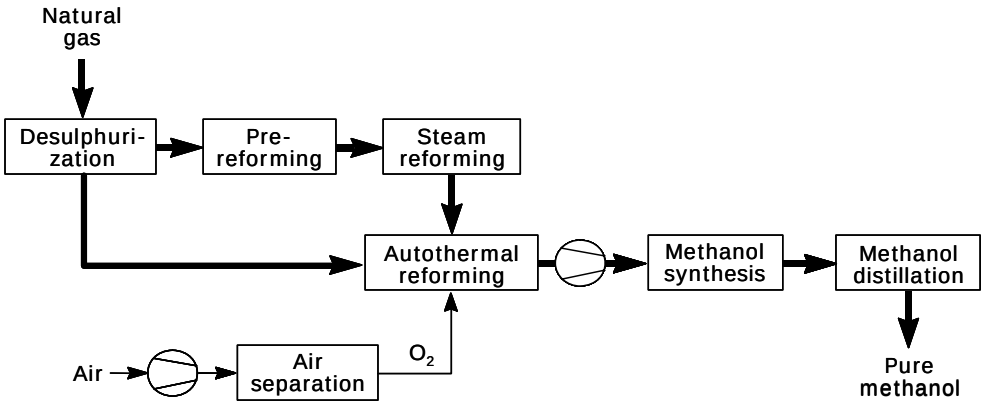


Figure 11: Methanol production with combined reforming [LURGI 2000]

4.1.3 Life cycle cost and energy balance

The investment costs for the whole plant are broken down as shown in **Table 9** according to [HANSEN et al. 1994]:

Table 9: Investment costs for a plant

Synthesis gas production and compression	**60%**
Methanol synthesis	10%
Distillation	10%
Other system components	20%

Total investment costs are dependent on the type and efficiency of the plant (according to [PEHNT 2001] the investment costs rise overproportionately with higher whole plant efficiencies), applicable environmental

and safety regulations, financing expenses and other boundary conditions. Total costs are essentially governed by synthesis gas production and treatment and the compression step preceding methanol synthesis.

Table 10: Balances for methanol supply from natural gas

Source	Methanol			Energy Chain	
	Energy demand /(GJ/t) [1]	Efficiency /(%)	CO_2 emissions /(kg/GJ) [1]	Efficiency of methanol supply /(%)	CO_2 emissions /(kg/GJ) [1]
[LURGI 1989]	30	66			
[SOLBAKKEN 1991]	32–29 [2]	62–69 [2]	23–15 [2]		
[HANSEN et al. 1994]	30.3	66			
[HÖHLEIN et al. 1995]	29	67	15		
[UHDE 1994]		68			
[WANG 2001]		68			
[GRUBE et al. 2001]		68	17	62	26
[PEHNT 1999], [PEHNT 2001]	30	66 [3]		60/58 [4]	24/27 [4]
[SPECHT 2002]		< 70			
[TES 2001]		≤ 68		≤ 62	27
[ADL 2000]		66			
[GREET 2002]		68			
[LURGI 2000]	28.5 [5]	70			

[1] /t, /GJ: methanol. [2] Comparison of conventional steam reforming (poor values) up to combined reforming and new processes (good values); potential for up to 30% decrease in investment costs for combined reforming and new processes; after [SOLBAKKEN 1991]; cf. [FITZPATRICK 2002]. [3] Higher efficiencies are possible at overproportionately higher investment costs. [4] Higher values for natural gas from CIS in comparison to natural gas from Norway. [5] Deviating unit: MMBtu/t; megaplants: methanol production > 5,000 t/d; decrease in production costs by about 25%; same efficiency as plants of 2,000–3,000 t/d [HAID 2001a] (cf. **Chapter 7.1.7 and Chapter 9**)

The results of a study comparison are shown in **Table 10**, specifying the efficiency and energy demand of the different methanol plants as well as the corresponding CO_2 emissions both for the plant and for natural gas supply and the plant. Theoretically, the energy balance based on the lower heating value for complete conversion of one methane molecule into one methanol molecule amounts to 80% (638 kJ/mol CH_3OH / 802 kJ/mol CH_4) or to 81.6% based on the upper heating value. For large methanol production plants based on natural gas (H. TOPSOE/DK, LURGI/D,

UHDED/D, KVAERNER/GB, etc.) data for the thermal energy balance can be found in the literature; unless otherwise specified, it is assumed that these data are based on the lower heating value, as is common practice in Europe.

The thermal efficiency for methanol production from natural gas may be up to 70% (based on lower heating value) for efficient processes with CO_2 emissions of about 16 kg_{CO2} / 2 $GJ_{methanol}$ (**Table 10**); decisive factors of influence are the process and the plant size (specific investment costs). The methanol production costs essentially depend on the cost of natural gas, which can be very different depending on the extraction region (USA, EU) and extraction conditions (remote gas) (cf. **Table 2**). All the other production paths based on other feedstocks (coal, waste, residual oils) are more expensive in terms of process engineering and involve higher CO_2 emissions; in case of the use of coal, CO_2 sequestration would even be required from the aspect of climate protection.

4.2 Methanol from coal

In comparison to the above-described conventional processes for methanol production from natural gas, the processes for the production of methanol or gasoline from coal by means of methanol synthesis (**Figure 12**) exhibit lower efficiencies and higher specific CO_2 emissions.

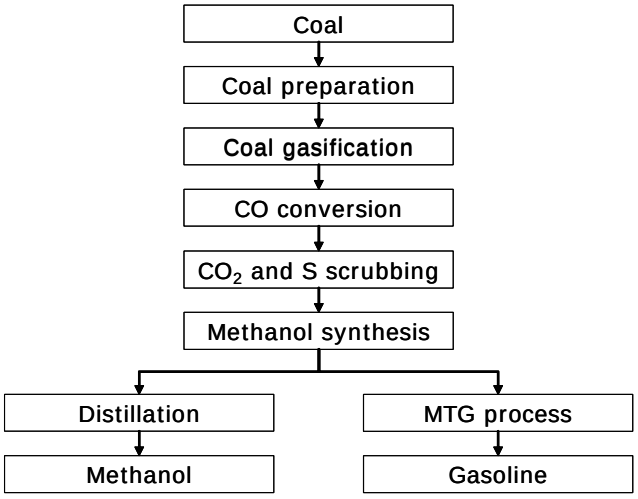


Figure 12: Process steps: methanol and gasoline from coal

The process of methanol production from coal requires extensive steps of coal preparation and synthesis gas treatment in addition to solid matter gasification prior to the actual methanol synthesis. Methanol synthesis is followed by distillation in accordance with the required product specification – fuel or chemical raw material. By means of the methanol-to-gasoline (MTG) process of LURGI it is also possible to produce gasoline fuel from methanol; this process competes with other methods of synthetic fuel production.

A detailed analysis of coal refinement in [SUPP 1990] compares the different processes of coal gasification with subsequent methanol production. It is found that the efficiencies for methanol supply are very different ranging (based on the upper heating value) from η = 0.4 for the Koppers-Totzek process up to η = 0.6 for the LURGI-BG-SLAGGER process. Optimizing the energy management was not taken into account here. The higher heating value (HHV) and the lower heating value (LHV) of water- and ash-free (waf) coal only differ by less than 5%.

An optimized process for methanol production from North Dakota lignite (30 $MJ_{HHV}/kg_{waf,\ coal}$ with 91 kg_{CO2}/GJ_{HHV}) requires after [SUPP 1990] 7,365 GJ/h coal (~ 245 t/h) for synthesis gas production in the LURGI dry bottom gasifier and 1,363 GJ/h coal (~ 45 t/h) for electricity and process heat production. In this way 4,833 GJ/h methanol (~ 213 t/h) is produced (22.7 $MJ_{HHV}/kg_{methanol}$). Without evaluating the byproducts this gives an efficiency of η_{HHV} = 0.55 with a specific emission rate of 116 $kg_{CO2}/GJ_{methanol}$.

Table 11: Potentials for methanol production from coal [SUPP 1990]

Gasification process		LURGI Dry Botom	LURGI BG *Slagger*	KOP-PERS-TOTZEK	SHELL	TEX-ACO	DOW
Coal input for gasification	/(kg_{coal}/kg_{CH3OH})	1.028	0.979	1.248	1.045	1.109	1.100
Coal input for O_2 and steam	/(kg_{coal}/kg_{CH3OH})	0.241	0.169	0.258	0.202	0.219	0.194
η_{Pseudo}	/(HHV_{CH3OH}/HHV_{coal})	0.542	0.599	0.406	0.552	0.518	0.532

HHV = higher heating value; η_{Pseudo} = without use of *waste heat* etc.

This value is about seven times higher than the comparable value for methanol production from natural gas, so that CO_2 sequestration would be required here. HILLER specifies in [HÄFELE 1990] an efficiency of η_{LHV} = 0.47–0.5 for methanol production from coal, without specifying the coal

and the respective coal gasification processes. **Table 11** shows the performance of different processes for methanol production from coal.

In the IKARUS report [HÖHLEIN et al. 1995] processes for methanol production from coal and residual oils were balanced as in **Table 12** (cf. also **Table 37**).

Table 12: Comparison of balances for methanol production from coal and residual oils and from natural gas (basis: LHV) [HÖHLEIN et al. 1995]

Process	Specific CO_2 emissions /($kg_{CO2}/GJ_{methanol}$)	Thermal efficiency /(%)
Methanol from natural gas	16	67
Methanol from hard coal (autothermal)	142	45
Methanol from hard coal (allothermal with nuclear high-temperature reactor / HTR)	53	38
Methanol from lignite (North Dakota)	116	48
Methanol from residual oil	38	56

4.3 Summary of Chapter 4

The efficiency (based on lower heating value) for methanol production from natural gas may be up to 70% depending on the process and plant size at different specific costs, emitting about 16 kg_{CO2} / $GJ_{methanol}$ (cf. **Table 37**). The investment costs are dependent on the efficiency of the plant and rise overproportionately with higher efficiencies of the whole plant. The total costs are governed by synthesis gas production and treatment and the compression step preceding methanol synthesis. The methanol production costs essentially depend on the cost of natural gas, which can be very different depending on the extraction region (USA, EU) and extraction conditions (remote gas). Production paths based on feedstocks other than natural gas (coal, residual oils) are more expensive in terms of process engineering; in the case of using coal, CO_2 sequestration would even be required from the aspect of climate protection. The use of biomass can reduce the specific CO_2 emissions of methanol supply (cf. also **Chapter 5, 6, 7** and **10**).

5 Synthesis gas [5]

5.1 Applications

5.1.1 Principles

Synthesis gas (syngas) is a mixture of hydrogen, carbon monoxide, and carbon dioxide. It may also contain nitrogen as applied for the ammonia synthesis. Syngas is a key intermediate in the chemical industry. It is used in a number of highly selective syntheses of a wide range of chemicals and fuels, and as a source of pure hydrogen and carbon monoxide.

The present use is primarily for the manufacture of ammonia (2000: 120 million t/y) and of methanol (2000: 30 million t/y) followed by the use of pure hydrogen for hydrotreating in refineries. Other applications are for synthesis of higher alcohols (by hydroformulation), hydrogenation of unsaturated compounds and direct reduction of iron ore.

Synthesis gas can be produced from almost any carbon source ranging from natural gas and oil products to coal and biomass by oxidation with steam and oxygen. Hence it represents a key for creating flexibility for the chemical industry and for the manufacture of *synthetic fuels* (synfuels).

In most plants, the heat is utilized for running the plant. This requires that the heat is available at sufficiently high temperature to raise high-pressure steam.

5.1.2 Natural gas conversion

The future use of syngas is dominated by the conversion of cheap natural gas into liquid fuels, *gas to liquids* (GTL). This is *natural gas at remote locations* (”stranded natural gas”) with no market for electricity and too far away to justify a pipeline. Another topic is a possible role of syngas technology in a future ”hydrogen economy” not the least associated with the use of fuel cells. These trends imply on the one hand the scale-up to very large-scale GTL plants (above 500,000 Nm^3_{syngas}/h) and on the other hand the

[5] Chapter 5 sources: figures after Rostrup-Nielsen (HTAS), 2005.

scale-down to small hydrogen units for fuel cells (5–100 Nm^3_{syngas}/h). This creates new challenges to the technology and the involved catalysis.

The conversion of natural GTL products has been discussed for decades and recently as a solution for the validation of ”stranded natural gas”, as the liquid fuels can be moved readily around the world to markets where they are most needed. So far, projects involving *liquified natural gas* (LNG) have typically proven to be more feasible. The gas conversion (GTL) has suffered from small price differential between the product and natural gas. The regulation prohibiting *flaring* of natural gas (typically associated gas at oil fields) as well as lower investments in the GTL plants has changed this picture. About 3% of the natural gas production is flared which corresponds to ca. 200 million t_{CO2}/y or about 0.7% of the total world CO_2 production. With flaring of natural gas being prohibited, the real price of natural gas at these remote areas may even be negative in view of the costs of reinjection in the oil fields.

The manufacture of synfuels via syngas was applied in Germany during World War II with nine plants based on *Fischer-Tropsch* (FT) synthesis with a total capacity amounting to 700,000 t/y (ca. 7,000 bpd). The syngas was made by coal gasification as also for the original FT units in South Africa (Sasolburg, Secunda). The manufacture of synfuels from natural gas is technically feasible as demonstrated by the *methanol to gasoline* (MTG) plant in New Zealand, and the FT units in Malaysia and Mossel Bay, South Africa. Further units are under design in Nigeria and Qatar by Sasol (each about 30,000 bpd). Shell has announced units in Qatar with a capacity of 70,000 bpd and recently Exxon Mobil announced another plant in Qatar with a capacity of 150,000 bpd.

Hydrogen is an energy carrier resulting in great flexibility as it can be manufactured from a variety of energy sources. In addition, the environmental prospects of a hydrogen economy are great. A hydrogen economy based on fossil fuels may well solve local environmental problems (smog, NOx etc.), but will still result in CO_2 missions. Hence, significant efforts are being made to develop technologies for hydrogen production based on fossil fuels combined with CO_2 sequestration. The aim is to develop effective methods to capture significant amounts of CO_2 from power generation and store the CO_2 in geological formations. **Figure 13** shows a scheme for large-scale power production based on air-blown reforming of natural gas coupled to CO_2 sequestration. It is essential that CO_2 is captured at as high a pressure as possible since CO_2 absorption from flue gas will be very energy requiring.

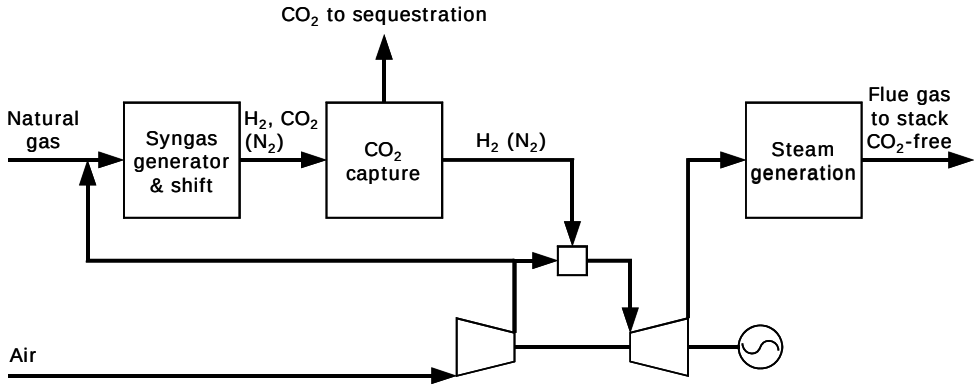


Figure 13: Hydrogen by air-blown reforming for CO_2-free power production [ROSTRUP-NIELSEN 2004]

If CO_2 sequestration is accepted, hydrogen could also be manufactured from coal via gasification with CO_2 sequestration, but fossil fuels remain an intermediate solution before cheaper solutions for hydrogen production methods on the basis of non-fossil fuels are developed.

5.1.3 Coal conversion

Coal conversion was considered before in the 1970s as a reaction to the oil crisis. The target was the manufacture of *substitute natural gas* (SNG) via coal gasification to syngas and methanation. SNG was never introduced at a large scale before oil prices decreased. The conversion of coal to liquid fuels was not feasible except in special circumstances (South Africa) because of the high investments in coal gasification.

Coal gasification was also applied in *integrated gasification combined cycle* (IGCC) power plants in which the ”syngas” was burned in a gas turbine followed by a steam turbine. These power plants had higher electric efficiencies than conventional coal-based power plants, but they were more expensive. At the same time, advanced schemes based on conventional technology were improved to efficiencies higher (49–50%$_{LHV}$ without CO_2 capture) than IGCC plants. Today, IGCC plants (Shell gasification) can be built with an electric efficiency of ca. 43%$_{LHV}$. However, because of the high gasification pressure (35–50 bar), they are more suited for CO_2 sequestration. With CO_2 capture, the efficiency falls to ca. 35% and the investments increase by one third.

Hydrogen as well as methanol (or *dimethyl ether* (DME) and FT diesel) can be produced cheaply in once-through synthesis as side products in IGCC plants. IGCC plants operate most efficiently at constant load and a side production of methanol or DME could be used as a buffer for load variations as shown in **Figure 14**.

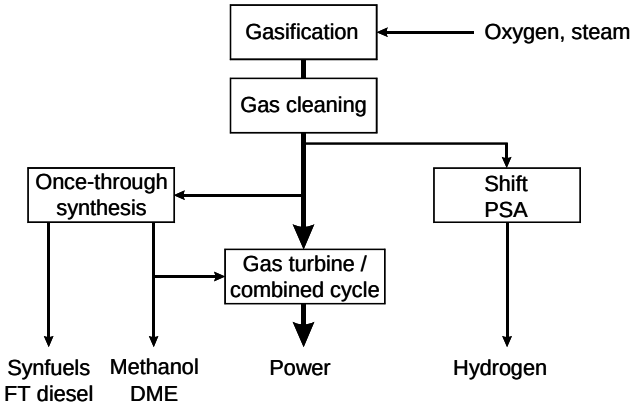


Figure 14: IGCC power plant combined with production of chemicals [ROSTRUP-NIELSEN 2004]

Hydrogen production from coal is considered in the US "Future Gen Program" as co-production in IGCC power plants as illustrated in **Figure 14**. In this way, coal and other heavy fossil fuels (tar sand, petrocoke) may again play an important role in the energy supply. Hydrogen, methanol and synfuels might be produced cheaply in once-through synthesis units if the non-converted syngas is used for power production. This is rarely the option for "stranded natural gas".

5.2 Synthesis gas technologies

Syngas is manufactured by a partial oxidation of the carbon-containing raw material. A number of technologies are applied and the choice depends on raw material and plant size. Natural gas and liquid hydrocarbons can be converted to syngas over a nickel catalyst by means of steam (and CO_2) by the synthesis gas reactions according to **Table 13**.

Table 13: Synthesis gas reactions for methane conversion [ROSTRUP-NIELSEN 2002a]

Process	Reaction	heat of reaction $-\Delta H^{o}_{298}$ / (kJ/mol)
Steam Reforming	1. $CH_4 + H_2O = CO + 3\ H_2$	-206
	2. $C_nH_m + n\ H_2O = n\ CO + (n+m/2)\ H_2$	-1175 *
	3. $CO + H_2O = CO_2 + H_2$	41
CO_2 Reforming	4. $CH_4 + CO_2 = 2\ CO + 2\ H_2$	-247
Autothermal Reforming (ATR)	5. $CH_4 + 1½\ O_2 = CO + 2\ H_2O$	520
	6. $CH_4 + H_2O = CO + 3\ H_2$	-206
	7. $CO + H_2O = CO_2 + H_2$	41
Catalytic Partial Oxidation (CPO)	8. $CH_4 + ½\ O_2 = CO + 2\ H_2$	38

* for nC_7H_{16}

5.2.1 Steam reforming

Steam reforming of methane is strongly endothermic. Therefore the steam reforming must be carried out at high temperature and low pressure to achieve maximum conversion as illustrated in **Figure 15**. The design of the steam reforming process is dictated by these constraints (*steam to carbon ratio* (s/c) cf. **Chapter 5.3.1**).

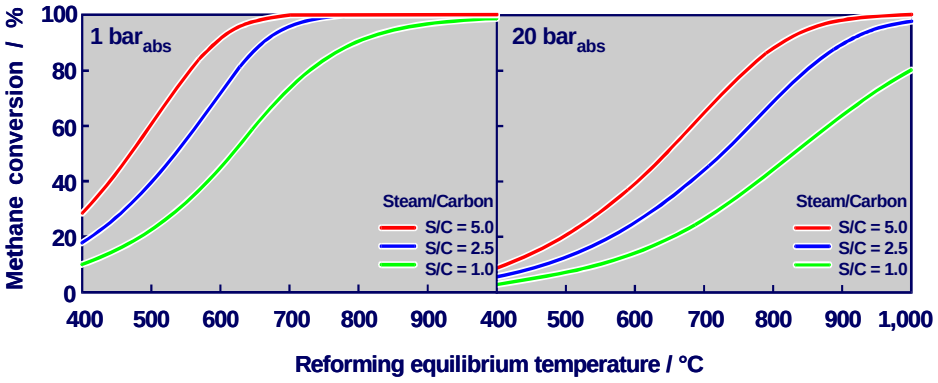


Figure 15: Steam reforming and methane conversion [ROSTRUP-NIELSEN 2002a]

In order to supply the heat for the overall endothermic steam reforming reaction, the catalyst is loaded into a number of high-alloy tubes placed inside a furnace equipped with burners. The industrial-size *tubular reformer* consists of a box-type radiant section including the burners and a convection section to recover the waste heat of the flue gas leaving the radiant section (**Figure 16**). Reforming tubes are placed in a row along the furnace. Typical inlet temperatures are 450–650°C, and the product gas leaves the reformer at equilibrium at the exit temperature of 700–950°C depending on the application.

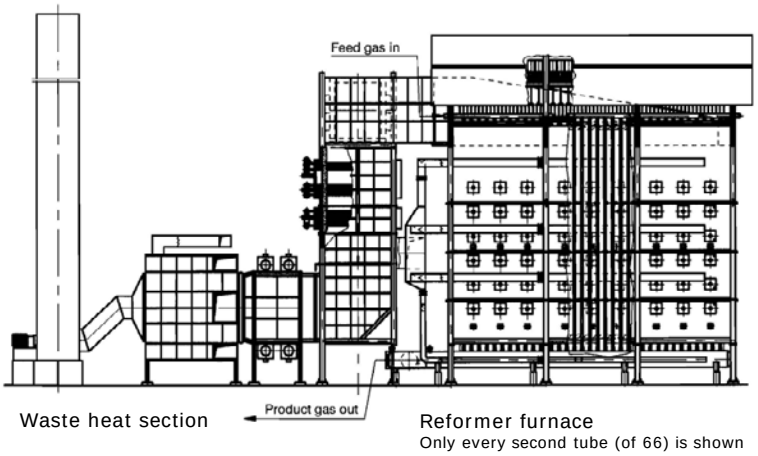


Figure 16: Reformer furnace. Waste heat section (Source: HTAS)

The steam reforming process may appear straightforward from an overall consideration as the product composition is determined by simple thermodynamics, but in reality it is a complex coupling of catalysis, heat transfer and mechanical design. In general, there has been progress in steam reforming technology resulting in less costly and more efficient plants – in part because of better materials for the reformer tubes, better control and understanding of carbon limits, better catalysts and process concepts with high feedstock flexibility.

Steam reforming of liquid hydrocarbons is also used for syngas production. With proper desulphurisation, it is possible to convert naphtha and heavy distillates such as kerosene and diesel in a prereformer into syngas with no trace of higher hydrocarbons. The limiting factor is the content of aromatics – and hence FT diesel being paraffinic and sulphur-free is as easily reformed as naphtha.

An alternative approach is to add oxygen to the feed and hence gain the necessary heat by internal combustion. Partial oxidation with oxygen can be carried out in three ways. The non-catalytic partial oxidation (Texaco, Shell) needs high temperature to ensure complete conversion of methane and to reduce soot formation. Some soot is normally formed and is removed in a separate soot scrubber system downstream the partial oxidation reactor. The thermal processes typically result in a product gas with H_2/CO = 1.7–1.8. Gasification of heavy oil fractions, coal and biomass may play an increasing role as these fractions are becoming more available because of falling demands.

The *autothermal reforming* (ATR) process is a hybrid of partial oxidation and steam reforming using a burner and a fixed catalyst bed for equilibration of the gas. This allows a decrease of the maximum temperature and hence the oxygen consumption can be lowered. Soot formation can be eliminated by the addition of a certain amount of steam to the feedstock and by special burner design. Steam can hardly be added to the thermal processes without the risk of increased soot formation because of the resulting lower temperature.

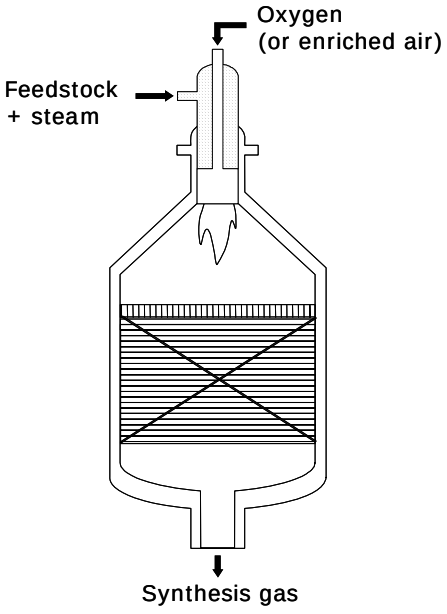


Figure 17: ATR reactor [CHRIST 1994]

The autothermal reformer is a simple piece of equipment with a special burner and a fixed catalyst bed in a brick-lined reactor shown in **Figure 17**. Irrespective of whether the burner is thermal or catalytic and whether a fixed or a fluidized catalyst bed is used, the product gas will be determined by the thermodynamic equilibrium at the exit temperature which itself is determined by the adiabatic heat balance.

In *catalytic partial oxidation* (CPO), the reactants are premixed and all chemical conversions take place in a catalytic reactor without burner. The direct CPO reaction (**Table 13**) appears as the ideal solution, since it provides a H_2/CO = 2 and has a low heat of reaction (38 kJ/mol). However, in practice, the reaction is accompanied by

the reforming and water gas shift reaction and at high conversions, the product gas will be close to thermodynamic equilibrium.

The steam reforming process requires a complex reactor, the tubular reformer, whereas the *partial oxidation* (POX) routes require an oxygen plant.

Up to 40% of the costs of a syngas plant based on ATR (CPO or POX) is related to the oxygen plant. As a result, *routes based on air* eliminating the cryogenic air separation plant have been suggested. The use of air in the process stream is possible only in once-through synthesis schemes to avoid a huge accumulation of nitrogen in the recyle loop. Attempts to use air instead of oxygen result in big gas volumes and consequently big feed/effluent heat exchangers and compressors. This is hardly feasible for large-scale plants. The use of *air-blown* autothermal reforming (or catalytic partial oxidation) is considered for the large-scale manufacture of hydrogen combined with CO_2 sequestration for power production (**Figure 13**). Its implementation will highly depend on imposed CO_2 legislation.

A cheaper technology for oxygen manufacture may be one route to reduce the costs of syngas manufacture. One attempt is to eliminate the oxygen plant and to include a reactor concept with oxygen addition through a *membrane*. With the strong driving force across the membrane, there is no need for compression of air to the process pressure. The feasibility is still to be proven.

5.2.2 CO_2 reforming

Steam reforming of light natural gas (*steam methane reforming* (SMR)) results in a *H_2/CO* ratio close to 3. Steam can be replaced by CO_2 resulting in a H_2/CO ratio close to 1. The H_2/CO ratio can be varied over a wider range as illustrated in **Figure 18** as the reforming reactions are coupled to the shift reaction. For the manufacture of hydrogen, the reforming process is followed by water gas shift carried out over copper catalysts at low temperatures (210–330^{o}C) to ensure complete conversion of carbon monoxide.

The choice of syngas technology is dictated by the need for high conversion, the requirements of the syngas composition, and by the scale of operation.

The requirement of the composition of the syngas varies with the synthesis in question as shown in **Table 14**.

The required *properties of the syngas* are different for the different syntheses. In the synthesis of methanol, DME and gasoline by TIGAS and in

the high temperature FT synthesis, CO_2 and CO are both reactants linked by the CO-shift reaction. This means that the synthesis gas ideally has the same stoichiometry as the final product. This is expressed by the *module* $M = (H_2\text{-}CO_2)/(CO+CO_2)$ which should be close to 2. In contrast, CO is the only reactant for the low temperature FT synthesis of wax and diesel since the cobalt catalyst is not active for the shift reaction and the optimum syngas composition is close to $H_2/CO = 2$.

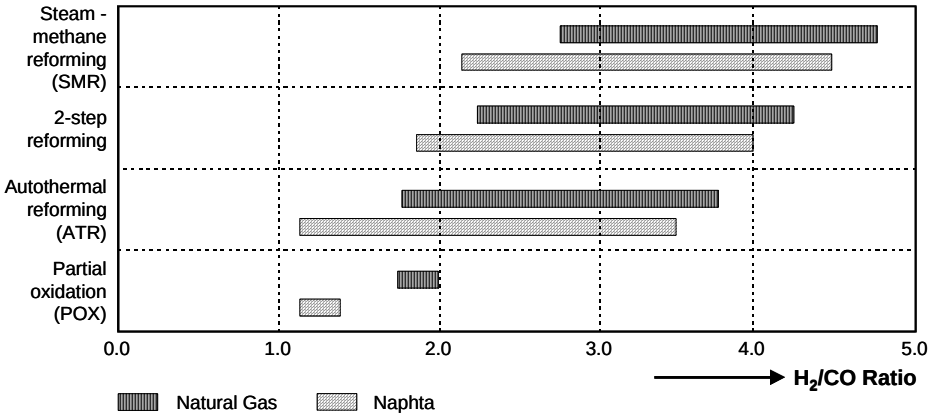


Figure 18: H_2/CO ratios from different syngas processes [ROSTRUP-NIELSEN 2002a]

Table 14: Syngas composition for various processes [ROSTRUP-NIELSEN 2002a]

Process /[Product]	Syngas Composition	Add. feedstock
Methanol/DME, High-temperature Fischer-Tropsch [gasoline via TIGAS 1]	$M = \frac{H_2 - CO_2}{CO + CO_2} = 2$	
Low-temperature Fischer-Tropsch	H_2/CO= ca. 2	
Carbonylation [acetic acid]	CO	methanol
Hydroformulation [higher alcohols]	$H_2/CO = 1$	olefins
[Industrial hydrogen for refineries]	99.99 H_2	
[Hydrogen for PEFC 2]	<50 ppm CO	
Reducing gas (iron ore)	$\frac{H_2O + CO_2}{H_2 + CO + CO_2 + H_2O} \leq 0.05$	

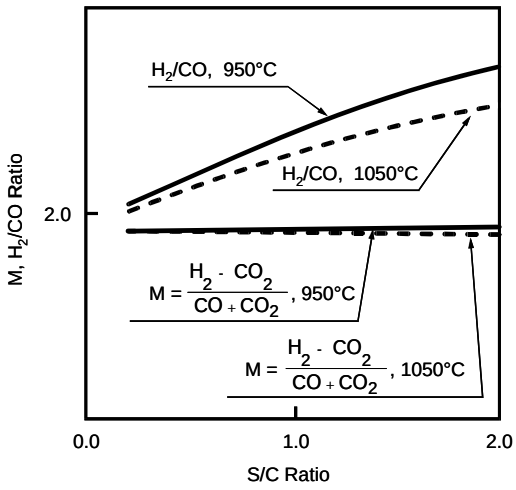
1 Topsøe integrated methanol/DME and gasoline synthesis [TOPP-JØRGENSEN 1987]
2 Polymer electrolyte fuel cell

5.3 Synthesis gas for methanol

5.3.1 Stoichiometry

The synthesis gas for methanol should ideally have the same stoichiometry as the final product. This is expressed by the module M which should be close to 2 as shown in **Table 14**: M = $(H_2-CO_2)/(CO+CO_2)$ = 2. M > 2 means too much, M < 2 means too little hydrogen in the syngas.

Figure 19 shows the H_2/CO ratio and the module M obtained from lean natural gas by ATR as function of the *steam to carbon ratio (S/C)* and the exit temperature. Although certain adjustments are possible, direct production by ATR of a gas with a module M = 2 is impossible. Such gases are best produced by a combination of steam reforming and oxygen-fired secondary reforming or, for very large capacities, by ATR followed by adjustment of the gas composition by the addition of H_2 and/or removal of CO_2 .



Feed preheat temperature 550°C, no prereformer.

Figure 19: Module M and H_2/CO in raw gas from ATR [CHRIST 1998]

Liquid hydrocarbons have a lower H/C ratio than CH_4 meaning less requirement of CO_2 for meeting the module M=2. The feasibility of CO_2 reforming depends strongly on the price (and pressure) of the CO_2 source. Many natural gas resources as well as biogas contain large quantities of CO_2.

5.3.2 Choice of technology

The choice of technology for the manufacture of synthesis gas depends on the scale of operation. For methanol, tubular reforming would be cheapest at a capacity below 1,000–1,500 MTPD, whereas the autothermal reforming is favoured at capacities above about 6,000 MTPD. This is caused by the economy of scale being different for the tubular reformer and the oxygen plant as illustrated in **Figure 20**.

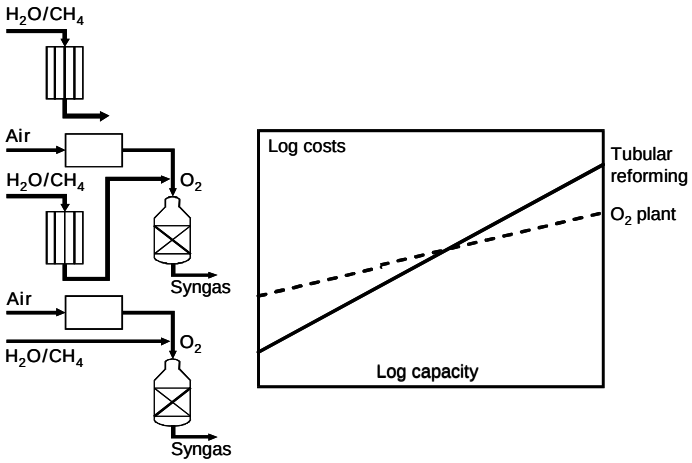


Figure 20: Impact of economy of scale [ROSTRUP-NIELSEN 2000a]

For the intermediate range representing the capacity of world-scale methanol plants, a combination of tubular reforming and a secondary oxygen-blown reformer is normally the optimum solution. **Figure 21** shows the two-step reforming unit in a 2,500 MTPD methanol plant.

Syngas with M=2 cannot be produced directly by steam reforming of natural gas. The surplus hydrogen is recycled to the reformer as fuel. However, combined steam and CO_2 reforming can meet the right stoichiometry. The reaction

$$¾\ CH_4 + ¼\ CO_2 + ½\ H_2O = CO + 2\ H_2 = CH_3OH$$

forms the basis for a recent 3,000 MTPD methanol plant in Iran.

Specific studies have been made on the use of ATR for synthesis gas production for very large methanol and FT plants. It was found that in no case does the ATR technology set the limit for the size of single-stream units. Capacities of about 10,000 MTPD methanol products can be ac-

commodated in one ATR reactor (but not necessarily by other parts of the plant, e.g. boilers, compressors, air separation units, etc.).

Desulphurisation and pre-reformer are placed to the right, and the secondary reformer to the left of the tubular reformer

Figure 21: Synthesis gas plant of 2,500 MTPD methanol plant, Statoil, Tjeldbergodden (Source: HTAS)

5.4 Direct conversion

It remains a challenge to find new routes for the direct conversion of methane into petrochemicals. Attempts to convert methane by direct oxidation into methanol have not been encouraging.

$$CH_4 \xrightarrow{\frac{1}{2}O_2} CH_3OH \xrightarrow{O_2} CO_2 + H_2O$$

High selectivities of about 90% may be achieved, but at low conversions per pass making it difficult to exceed a yield per pass above 5%. As illustrated in **Figure 22** a selectivity of 95% at a conversion of 5% means a large recycle ratio of ca. 10, and hence a difficult separation due to low partial pressure of the product.

In comparison, the commercial syngas-based methanol synthesis has a conversion per pass of 50% and a total recycle ratio of 4, using the recycle to control the temperature in the reactor. This does not harm the economy, because the selectivity is 99.9% meaning a yield per pass close to 50%.

High selectivity and conversion may not be sufficient. A process (Catalytica) for converting CH_4 via methyl bi-sulphate into methanol has the potential of achieving a high selectivity of 95% at a conversion of 90%. However, the process would require a large sulphuric acid plant

($1\ mol_{SO2}/mol_{methanol}$) and a unit for concentrating a large recycle of dilute acid.

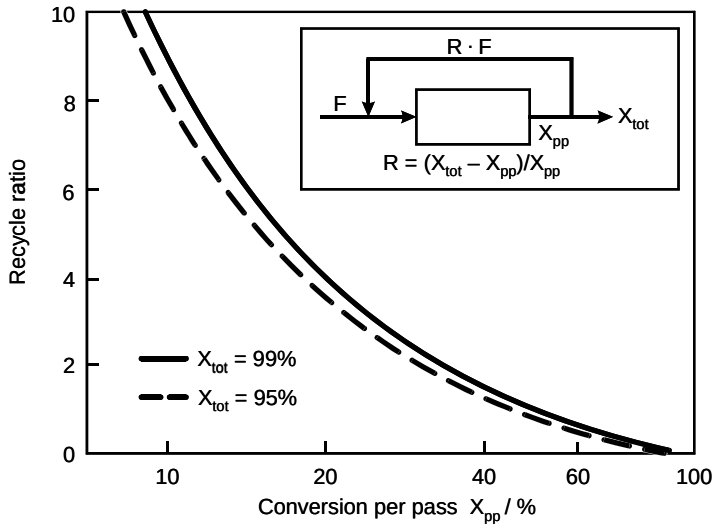


Figure 22: Recycle ratio and conversion [ROSTRUP-NIELSEN 2000b]

A syngas-based route has often been characterised as being inefficient. In fact, syngas manufacture is very efficient. The thermal efficiency of a tubular reformer approaches 95%, as most of the heat input to the process is recovered from the flue gas and the product stream. The main advantage of the indirect routes via syngas is the very high *carbon efficiency*, but it involves a high exchange of energy and thereby high capital costs.

5.5 Summary of Chapter 5

Synthesis gas (syngas) can be produced from almost any carbon source ranging from natural gas and oil products to coal and biomass via reforming or gasification processes. It represents a key for creating flexibility for the chemical industry and for the manufacture of synthetic fuels. The future use of syngas is dominated by the conversion of cheap natural gas into liquid fuels, *gas to liquids* (GTL). Another way may be manufacturing a *substitute natural gas* (SNG) via coal gasification to syngas and subsequent methanation. Coal gasification was also applied in *integrated gasification combined cycle* (IGCC) power plants. Syngas is manufactured by a partial oxidation of the carbon-containing raw material. A number of technologies are applied such as steam reforming or CO_2 reforming. The required *prop-*

erties of the syngas are different for the different syntheses. This means that the synthesis gas ideally has the same stoichiometry as the final product. The synthesis gas for methanol should ideally have a module M which should be close to 2. The choice of technology for the manufacture of synthesis gas depends on the scale of operation. Large capacities of methanol products can be accommodated in one ATR reactor. The main advantage of the indirect routes for methanol production via syngas is the very high *carbon efficiency*, but it involves a high exchange of energy and thereby high capital costs.

6 Process engineering of methanol synthesis

6.1 Methanol production technology

All commercially used methanol technologies call for three process units and a utility section as listed below:

– synthesis gas preparation (reforming),

– methanol synthesis,

– methanol purification,

– utilities.

In the synthesis gas preparation section, the hydrocarbon feedstock is purified of for instance sulphur before being converted into synthesis gas at high temperature and subsequently compressed to synthesis pressure. Several reforming technologies are available for gas conversion, e.g.:

– one-step reforming with a tubular reformer,

– two-step reforming,

– autothermal reforming (ATR).

In the methanol synthesis section, the synthesis gas is converted to raw methanol, which contains water and minor amounts of by-products. The straight-tubed boiling water reactor (BWR) is often used being the most efficient reactor type. For large capacities more than one reactor is required and economy of scale may be lost. In this case three adiabatic methanol reactors in series with indirect cooling between the reactors may be attractive.

Water and by-products are removed in the methanol distillation section. The conventional layout is with a two-column system (stabiliser for dissolved gases and light by-products and concentration column separating methanol and water). The Topsøe system features a split concentration column and an optional ethanol column. The first column operates at higher pressure. This allows the overhead condenser duty to be reused as reboiler duty for the second column – leading to a saving in overall energy consumption.

The *utility* section comprises water treatment, cooling water system, auxiliary boiler, power production, and other installations as required for the proper operation of the plant.

A comprehensive survey of methanol production technology is given in [HANSEN 1997]. Discussions of process alternatives may be found in ([HOLM-LARSEN 1994], [DYBKJÆR et al. 1997]).

In the design of a methanol plant, the process sections may be considered independently and the technology may be selected and optimised separately for each section. The normal criteria for the selection of technology are capital cost and process efficiency. At remote sites, the focus is normally on capital cost, whereas process efficiency generally has higher priority at sites with developed infrastructure. With respect to overall energy consumption about 80% (measured as carbon retention) is consumed in the reforming section. Furthermore, the reforming section alone accounts for more than about 60% of the investment. Therefore it is obvious that the selection of reforming technology is of paramount importance, regardless of the site.

Typical capacities for world-scale methanol plants have been in the range of 1,500–2,500 MTPD. Lately, the trend has been to obtain lower production costs by building even larger plants to achieve economy of scale.

6.2 Synthesis gas preparation [6]

Often referred to as module M, the methanol synthesis gas is characterised by the stoichiometric ratio $(H_2-CO_2)/(CO+CO_2)$. A module of 2 defines a stoichiometric synthesis gas with respect to the formation of methanol. Sub-stoichiometric synthesis gas should be avoided due to increased risk of by-product formation. Slightly over-stoichiometric synthesis gas is preferred since a high hydrogen partial pressure leads to high reaction rate and high carbon efficiency in the synthesis loop.

Other important properties of the synthesis gas are the $CO:CO_2$ ratio and the concentration of inerts. A high $CO:CO_2$ ratio will increase the reaction rate and the achievable per pass conversion. In addition, the formation of water will decrease, decreasing the catalyst deactivation rate. The presence of inerts will lower the partial pressure of the active reactants. Inerts in methanol synthesis are methane, argon and nitrogen.

The following paragraphs contain an overview of different synthesis gas preparation technologies. The focus will be on issues related specifically to methanol synthesis. For a general description of the synthesis gas genera-

[6] Chapter 6.2 sources: figures after Dybkjær/Nørgaard/Perregaard (HTAS), 2005.

tion technologies, please refer to **Chapter 5** and to [AASBERG-PETERSEN et al. 2004].

In the following, the synthesis gas passing from the synthesis gas preparation section to the synthesis loop is referred to as “make-up gas”. The “recycle gas” is the gas which is returned to the synthesis reactor after separation of raw product in the product separator, and the “purge gas” is the gas withdrawn from the synthesis loop to remove excess reactants (mainly hydrogen) and to prevent the build-up of inerts (mainly methane, nitrogen, and argon). The “converter feed” is the mixture of make-up gas and recycle gas.

6.2.1 One-step reforming

In one-step reforming, the synthesis gas is produced by tubular steam reforming alone (without the use of oxygen). This concept was traditionally dominating. Today it is mainly considered for up to 2,500 MTPD plants and for cases where CO_2 is contained in the natural gas or available on site from other sources.

Natural gas feedstock is reformed in a tubular reformer under conditions leading to a reasonable low leakage of unconverted methane from the reformer (high temperature and relatively low pressure). The composition of the synthesis gas obtainable with this technology is determined by the ratio of carbon to hydrogen in the feedstock, and is only adjustable within a narrow range. A typical natural gas will produce a surplus of hydrogen of about 40%. This hydrogen is carried more or less as an inert through the synthesis section only to be purged and used as reformer fuel.

The addition of CO_2 permits optimisation of the synthesis gas composition for methanol production. CO_2 constitutes a less expensive feedstock, and CO_2 emission to the environment is reduced. CO_2 is also easier to reform than natural gas, leading to energy and investment savings under the right circumstances.

The application of CO_2 reforming results in a very energy-efficient plant with an energy consumption 5–10% less than of a conventional plant [HOLM-LARSEN 2000].

In one-step reforming, all the energy-consuming reforming reactions are accomplished in the tubular steam reformer, and this requires a large radiant section in the reformer with a large flow of hot flue gas from the radiant section. As a result, a substantial heat surplus is found in the conversion section of the furnace, leading to steam surplus. The steam sur-

plus can be reduced by the application of combustion air preheat, adiabatic prereforming or (most likely) a combination.

A simplified process flow diagram for a methanol plant based on single-step reforming is shown in **Figure 23**.

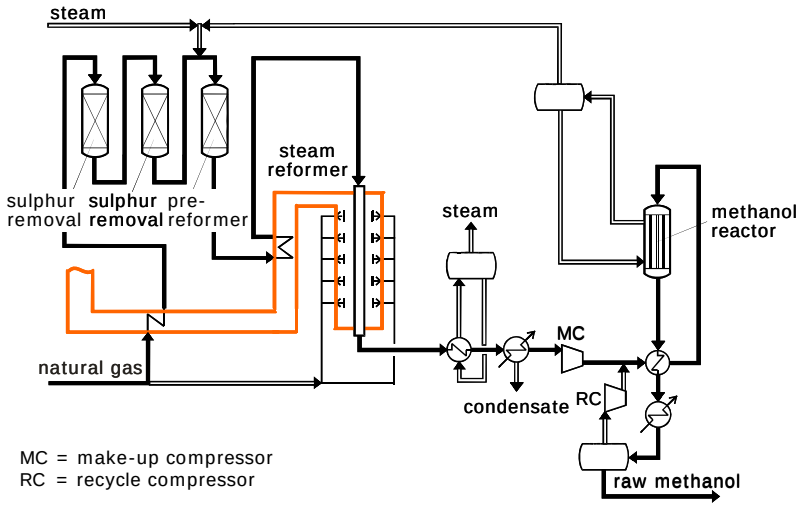


Figure 23: Methanol production by one-step reforming – simplified process flow diagram

A 3,030 MTPD methanol plant based on CO_2 reforming was started up in Iran in 2004.

Convective steam reforming has been commercialised for hydrogen and carbon monoxide production [DYBKJÆR et al. 2004]. A convective reformer produces a synthesis gas similar to the gas produced in a tubular steam reformer. Due to the compactness of the convective steam reformer technology and the elimination of the need for a multi-burner furnace, this technology is relevant for off-shore methanol production.

6.2.2 Two-step reforming

Two-step reforming features a combination of tubular reforming (primary reforming) and oxygen-fired secondary reforming. This combination resembles the typical reforming concept in ammonia plants except that the process air is substituted by an oxygen/steam mixture.

Stand-alone oxygen-fired reforming inherently produces a synthesis gas with a 15–20% deficiency in hydrogen, but by combining the two reforming technologies, tubular and oxygen-fired, it is possible to adjust the syn-

thesis gas to the most suitable composition for methanol synthesis (M slightly above 2.0).

The secondary reformer requires that the primary reformer is operated with a significant leakage of unconverted methane (methane slip). Typically 35–45% of the reforming reaction occurs in the tubular reformer, the rest in the oxygen-fired reformer. As a consequence, the tubular reformer can be operated under much less demanding conditions, i.e. lower steam to carbon ratio, lower temperature and higher pressure. These conditions combined with the reduction of duty to 35–40% lead to a reduction in reformer tube weight by 75–80%.

For rich natural gas or even heavier feedstock a prereformer may be installed upstream the tubular steam reformer. For lean natural gas, the fired duty in the tubular reformer is insufficient to supply the additional preheat that can be achieved by installing a prereformer. Consequently, the prereformer is not feasible for lean natural gas feed. In two-step reforming, the load on the hydrogen generating tubular steam reformer can be balanced against the load on the carbon oxide generating secondary reformer to obtain a stoichiometric synthesis gas.

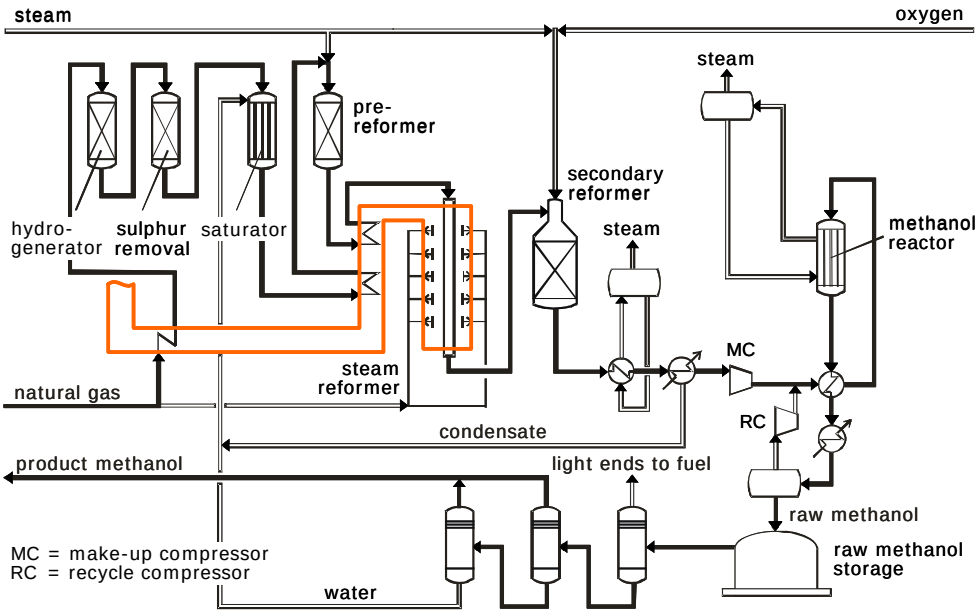


Figure 24: Methanol production by two-step reforming – simplified process flow diagram

A process flow diagram for a plant based on two-step reforming is shown in **Figure 24**.

The two-step reforming layout is used in a 2,400 MTPD methanol plant in Norway ([GEDDE-DAHL et al. 1998], [GEDDE-DAHL et al. 1999]). The plant was started up in 1997. It features in addition to the two-step reforming layout a number of technologies and operating parameters never demonstrated before in a world-scale grassroots methanol plant such as:

– falling film saturator,
– prereforming,
– three-column distillation.

6.2.3 Autothermal reforming

Autothermal reforming (ATR) features a stand-alone, oxygen-fired reformer. The primary tubular reformer is completely omitted, process layout is simplified, and plot area and construction cost are reduced as a result of the compactness of the design.

The autothermal reformer produces a synthesis gas that is rich in carbon monoxide, resulting in high reactivity of the gas. The synthesis gas is deficient in hydrogen, i.e. the gas outlet of the autothermal reformer has a module of 1.7–1.8. The module must be adjusted to a value of 2 before the synthesis gas is suitable for methanol production. The synthesis gas can be adjusted either by removing carbon dioxide from the synthesis gas or by recovering hydrogen from the methanol synthesis loop purge gas and recycling the recovered hydrogen to the synthesis gas [HAUGAARD 1999].

If the ATR is operated at low steam to carbon (S/C) ratio, this process scheme may produce a stoichiometric gas with a very low CO_2 content, very suitable for DME production, but too reactive for methanol synthesis.

Adjustment by hydrogen recovery can be done either by a membrane or a PSA unit. Membranes are relatively cheap and easy to operate and maintain. However, the hydrogen is recovered at low pressure and needs to be recompressed. The PSA unit is more complicated to operate, but the hydrogen is recovered at high pressure. Both solutions for hydrogen recovery are used in the industry.

A process flow diagram for a plant based on ATR with adjustment of the synthesis gas composition by hydrogen recovery in a membrane unit is shown in **Figure 25**.

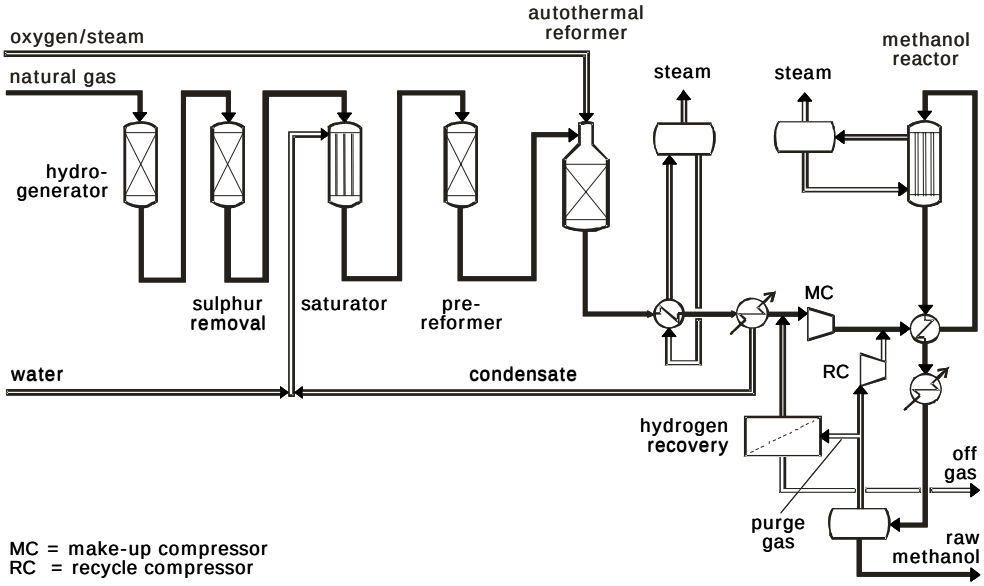


Figure 25: Methanol production by ATR at low S/C ratio. Adjustment of synthesis gas composition by hydrogen recovery and recycling. Simplified flow diagram.

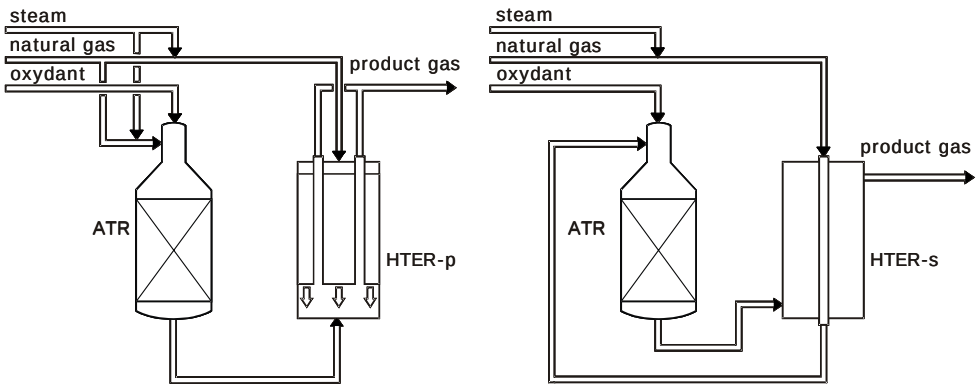
As shown in **Figure 25**, a prereformer is normally installed upstream the ATR to reduce oxygen consumption and increase the module, thereby reducing the amount of recovered and recycled hydrogen.

6.2.4 Gas-heated reforming

To overcome the problems associated with the hydrogen-deficient synthesis gas produced in the autothermal reformer, a gas-heated reformer (HTER, Haldor Topsøe Exchanger Reformer, or similar designs) may be installed in parallel (-p) or series (-s) with the autothermal reformer. The concepts are illustrated in **Figure 26** [BAKKERUD et al. 2004].

The gas-heated reformer will introduce a degree of steam reforming to the process hereby generating more hydrogen. In the extreme, the process is changed to a concept equivalent to two-step reforming, but with the heat for the steam reforming supplied by heat exchange with the hot gas from the ATR.

Gas-heated reforming holds the potential to increase the efficiency of the autothermal process without compromising its ability to produce a highly reactive synthesis gas at low steam to carbon ratio and high single-line capacity.



HTER: Haldor Topsøe exchanger reformer
-p / -s: installation in parallel / series

Figure 26: Gas-heated reforming in combination with ATR

Gas-heated reforming is commercialised in a parallel solution operating at high steam to carbon ratio [LOOCK et al. 2005]. This solution may be of interest as a revamp option. In a new plant a series solution operating at low steam to carbon ratio will be more attractive.

6.2.5 Choice between reforming technologies

Tubular steam reforming technology is mainly used in relatively small methanol plants up to 2,500 MTPD. For larger-scale plants the tubular steam reformer technology will have to be constructed in multiple production lines hereby losing the economy of scale compared to the oxygen-fired technologies. The availability of CO_2 increases the capacity range where one-step reforming is attractive.

Two-step reforming is attractive in a capacity range starting at approximately 2,000 MTPD and up to approximately 7,000 MTPD depending on feedstock. Above approximately 7,000 MTPD two-step becomes less attractive due to poor economy of scale of the tubular reformer above this capacity. The availability of CO_2 is no advantage with two-step reforming.

Autothermal reforming is feasible for large-scale methanol plants. The ability to operate at a steam to carbon ratio of 0.6 or lower enables the technology to achieve a single-line capacity of at least 10,000 MTPD of methanol. Natural gas with a high content of higher hydrocarbons (“heavy natural gas”) makes ATR less attractive. The availability of CO_2 is no advantage with ATR. The scheme is mainly attractive for the production of

fuel-grade methanol or for the production of feed for olefins production (MTO, methanol to olefins).

6.2.6 Gasification

Synthesis gas may also be prepared by partial oxidation or gasification of residual oil fractions, coal or other carbon sources.

Gasification may take place at pressures of up to 8.0 MPa, hereby saving the expensive synthesis gas compression. The module of the synthesis gas is very low (<1.5) and a carbon dioxide removal unit is necessary for adjustment of the module prior to admission of the gas to the synthesis loop. The result is a very aggressive synthesis gas mainly suitable for the production of fuel-grade methanol.

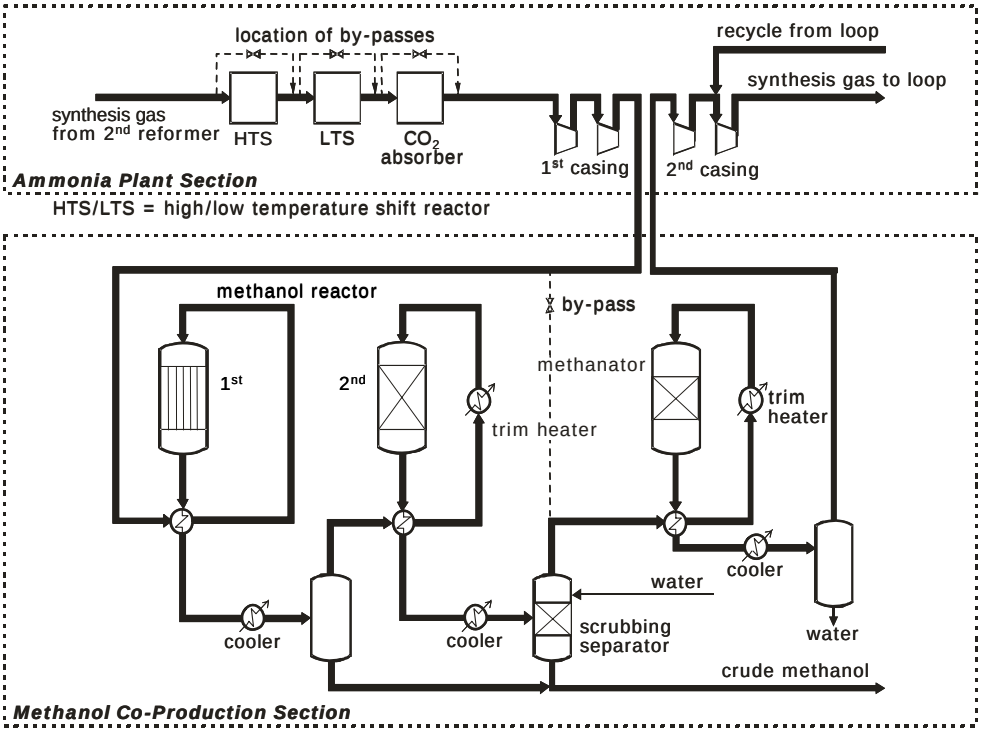


Figure 27: Co-production of methanol in ammonia plant. In-line facility. Simplified flow diagram

6.2.7 Co-production of methanol in ammonia plants

In certain cases it is interesting for ammonia plant owners to convert part of their capacity to methanol production. Besides adding flexibility, the co-production unit is compact, fast to install and low in investment. Several options are available for the integration of methanol production in existing or new ammonia plants:

– purge-gas-based facility; utilising hydrogen from the ammonia loop purge gas and carbon dioxide from the front-end,
– side stream facility; where the methanol reactor operates in parallel with the ammonia plant shift reactors,
– in-line facility; using the ammonia make-up gas compressor to obtain the desired methanol reactor pressure.

An in-line facility has been implemented at the ammonia/methanol co-production plant, Malaysia [HOLM-LARSEN 2000]. A simplified process flow diagram is shown in **Figure 27**.

6.3 Methanol synthesis [7]

In methanol synthesis, conversion of synthesis gas into raw methanol takes place. Raw methanol is a mixture of methanol, water and by-products, predominantly higher alcohols, ethers, acetone and methyl-ethyl-ketone.

6.3.1 Thermodynamics

The conversion in methanol synthesis can be described by the following reactions:

$CO_2 + 3\ H_2 \Leftrightarrow CH_3OH + H_2O$ $(-\Delta H_{298K,\ 50bar} = 40.9\ kJ/mol)$ eq. 6.1

$CO + 2\ H_2 \Leftrightarrow CH_3OH$ $(-\Delta H_{298K,\ 50bar} = 90.7\ kJ/mol)$ eq. 6.2

$CO_2 + H_2 \Leftrightarrow CO + H_2O$ $(-\Delta H_{298K,\ 50bar} = 49.8\ kJ/mol)$ eq. 6.3

A combination of either **equations 6.1** and **6.3** or **equations 6.2** and **6.3** completely describes the system from a thermodynamic point of view, whereas all three equations are generally considered when a kinetic description of the synthesis is required.

[7] Chapter 6.3 sources: figures after Dybkjær/Nørgaard/Perregaard (HTAS), 2005.

It can be seen from **equations 6.1**, **6.2** and **6.3** that the methanol synthesis is exothermic and involves a decrease in the number of moles. Thus, according to Le Chatelier's principle, maximum conversion is obtained at low temperature and high pressure. A challenge in the design of a methanol synthesis is to remove the heat of reaction efficiently and economically – i.e. at high temperature – but at the same time equilibrating the synthesis reaction at low temperature hereby ensuring a high per pass conversion.

Inerts like CH_4, N_2 or Ar lower the possible conversion. It is noted that even in a stoichiometric synthesis gas free from inerts, maximum conversion will decrease with increasing CO_2 content. Under typical synthesis conditions (7.5 MPa, 225 °C) the carbon conversion (conversion of carbon oxides to methanol) per pass in traditional gas phase reactors can not exceed the thermodynamic limit around 60%.

6.3.2 Catalysts

The first industrial production of methanol was performed at high pressure using catalysts consisting of zinc oxide and chromium oxide. These catalysts were very stable towards catalyst poisons such as sulphur and chlorine components, which were often present in the synthesis gas at that time.

Developments in gas cleaning technologies allowed the use of the much more active and selective catalyst based on copper and zinc oxide identified by BASF in the 1920s. This resulted in the low-pressure methanol synthesis first used by ICI in the 1960s.

Today, the synthesis of methanol is almost exclusively performed over catalyst based on copper/zinc/alumina.

6.3.3 Reaction mechanism

The reaction mechanism for the low-temperature methanol synthesis catalyst is still debated and controversial. The main points in the debate are whether or not methanol is exclusively produced from CO_2 or whether the direct formation of methanol from CO is also possible.

Great efforts have been made to understand the mechanism and an overwhelming amount of information exists in the literature (cf. e.g. [HANSEN 1997]). A key in understanding is the adsorption properties of the different species as well as the surface components that can be identified. A number of different analytical techniques have been used (*IR*, *DRIFTS*,

TDS, *TPD*, etc.). **Figure 28** shows the most important species found on the surface.

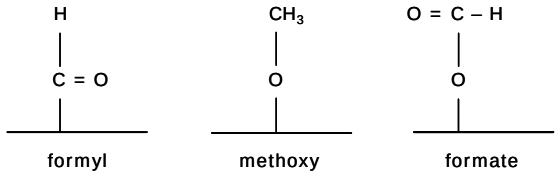


Figure 28: Most abundant surface species found on methanol synthesis catalysts

Formyl can be formed from CO and H_2 and is rapidly hydrogenated to methoxy species. Formate is by far the most dominant of the surface species identified. It can be formed from CO_2 and H_2. It is believed that the methanol synthesis occurs from surface formates and methoxy species and that the most likely rate-determining step is the hydrogenation of adsorbed H_2COO to a methoxy species. As a comment on the debate of the formation of methanol from CO and/or CO_2, it seems that both molecules via different reaction pathways can give rise to the final surface species, the methoxy group. Thus, it is likely that both pathways exist and are more or less active depending on the operating conditions as well as the state of the surface of the catalyst.

6.3.4 Kinetics

When considering the kinetics of the methanol synthesis it is necessary that the shift reaction is also considered. A model that does not take both the synthesis and the shift reaction into account is of very limited value. Also, as discussed above, one should evaluate whether both syntheses from CO and CO_2 should be part of the model.

Lately, the approach of using microkinetic models has gained in importance and has also been applied to the methanol synthesis and shift reaction [ASKGAARD et al. 1995]. Microkinetic models are based on *UHV* measurements on well-defined single crystals. The elementary steps are shown in **Table 15**. An asterisk (*) means an empty active site on the surface.

Step 7 is assumed to be the rate-limiting step for the shift reaction, whereas step 11 is the rate-limiting step for the methanol synthesis as explained above. It is noted that even when data from single-crystal experiments is combined with standard gas phase thermodynamic data only

minor deviation between the microkinetic model and data under industrial conditions is seen. The model predicts coverage of around 50% (primarily H_2 coverage). It is noteworthy that the model predicts that the surface of the catalyst becomes nearly 100% covered with the formate surface species at low temperature. Thus, the methanol synthesis reaction is self-inhibiting at low temperature and at high CO_2 concentration.

Table 15: Elementary steps of the microkinetic model

Step	Reaction
1	$H_2O(g) + * \Leftrightarrow H_2O*$
2	$H_2O* + * \Leftrightarrow OH* + H*$
3	$2\ OH* \Leftrightarrow H_2O* + O*$
4	$OH* \Leftrightarrow O* + H*$
5	$2\ H* \Leftrightarrow H_2(g) + 2\ *$
6	$CO(g) + * \Leftrightarrow CO*$
7	$CO* + O* \Leftrightarrow CO_2* + *$

* = empty active site on the surface

Step	Reaction
8	$CO_2\,(g) + * \Leftrightarrow CO_2\,*$
9	$CO_2* + H* \Leftrightarrow HCOO* + *$
10	$HCOO* + H* \Leftrightarrow H_2COO* + *$
11	$H_2COO* + H* \Leftrightarrow H_3CO* + O*$
12	$H_3CO* + H* \Leftrightarrow CH_3OH* + *$
13	$CH_3OH* \Leftrightarrow CH_3OH(g)$

* = empty active site on the surface

The activation energy is in the order of 75–100 kJ/mol in accordance with what is observed in industry and the reaction orders are CO_2=1, CO≈0 and H_2=1–2.

The industrially proven water inhibition is explained by site blocking in the classic Langmuir-Hinshelwood types of reaction rate expression. This effect is one of the main explanations why synthesis gas with low CO_2 and thus low formation of water is much more reactive than synthesis gas with high CO_2. However, part of the explanation is also believed to be the contribution of the direct synthesis from CO.

6.3.5 By-products

Generally, the methanol synthesis catalyst and process is highly selective, and selectivity of 99.9% is not uncommon. This is truly remarkable, in particular when it is considered that the by-products normally found are thermodynamically more favoured than methanol.

The by-products include:

– higher alcohols (ethanol, propanols and butanols),

– esters (methyl formate and methyl acetate),
– ethers (dimethyl ether),
– ketones (acetone and methyl ethyl ketones),
– hydrocarbons as normal alkanes,
– minor amounts of acids and aldehyde.

In **Table 16** some typical figures for the by-product formation level are shown.

Table 16: Typical by-product formation [HANSEN 1990]

Parameter	Gas type	
	CO-rich	CO_2-rich
T_{inlet} / °C	197	197
T_{outlet} / °C	295	296
$CO:H_2$	0.33	0.16
$CO:CO_2$	3.52	0.80
Ethanol / (ppmw)	2,840	287
Propanols / (ppmw)	921	166
Butanols / (ppmw)	651	110
Acetone / (ppmw)	48	<5
MEK [1] / (ppmw)	83	<5

[1] MEK: methyl ethyl ketones

6.3.6 Design of methanol synthesis reactors

Many different designs of methanol synthesis reactors have been suggested. The following paragraphs will shortly highlight the main features of the most important designs. For more detailed reviews reference is made to ([NITROGEN 1994], [TIJM et al. 2001]).

6.3.6.1 Quench reactor

A quench reactor consists of a number of adiabatic catalyst beds installed in series in a common pressure shell. The reactor feed is split into several fractions and distributed to the synthesis reactor between the individual catalyst beds. I.e. instead of removing the heat from the system the reaction temperature is controlled by stepwise addition of reactor feedstock.

The resulting reactor design is very simple and consequently features a low investment. However, catalyst utilisation is poor as not all the reac-

tants pass through the entire catalyst volume installed. The adiabatic nature of the design implies that the equilibrium temperature is high resulting in a low per pass conversion. The lack of internal or inter-stage cooling results in an inefficient heat recovery. Most of the generated heat must be removed by air or water cooling.

6.3.6.2 Adiabatic reactor

An adiabatic reactor system normally consists of a number of fixed-bed synthesis reactors placed in series. Heat is removed downstream each reactor by the generation of medium-pressure steam.

An adiabatic reactor system features a good economy of scale. Mechanical simplicity gives a low investment cost. The fixed-bed reactor design can be scaled up to single-line capacities of 10,000 MTPD. However, due the adiabatic nature of the system the equilibrium temperature is high resulting in a low per pass conversion and high recycle ratio. The high recycle ratio dilutes the reactants resulting in high catalyst volumes. Thus, the efficiency of the adiabatic reactor system is low compared to systems with internal cooling. Reference is made to [HOLM-LARSEN 1994].

6.3.6.3 Boiling water reactor

The boiling water reactor is in principle a shell and tube heat exchanger with catalyst on the tube side. Cooling of the reactor is provided by circulating boiling water on the shell side. By controlling the pressure of the circulating boiling water the reaction temperature may be controlled and optimised easily.

The approximately isothermal nature of the reactor design gives a high conversion compared to the amount of catalyst installed. However, to ensure a proper reaction rate the reactor will operate at intermediate temperatures – say between 240ºC and 260ºC – and consequently the recycle ratio may still be significant.

Complex mechanical design results in relatively high investment cost. Moreover, the tube sheet constrains the maximum size of the synthesis reactor. Thus, for large-scale plants several boiling water reactors must be installed in parallel, thus eliminating the economy of scale.

6.3.6.4 Gas-cooled reactor

The gas-cooled reactor design is often designed into a feed/effluent heat exchanger around a boiling water reactor. I.e. on one side of the heat exchanger the boiling water reactor feed is preheated while on the other side of the heat exchanger catalyst is installed and the boiling water reactor ef-

fluent is brought to equilibrium at a lower temperature. With a gas-cooled reactor in series with a boiling water reactor very high per pass conversions may be achieved. However, due to the low temperature in the gas-cooled reactor the reaction rate is low and the amount of catalyst needed to make the reaction occur is correspondingly high.

6.3.6.5 Integrated gas-cooled reactor

An integrated design of the boiling water reactor and the gas-cooled reactor is also available. The design is similar to the boiling water reactor except that feed gas is heated in centre tubes placed in the catalyst tube in the boiling water reactor. In terms of efficiency, the design is an intermediate between the pure boiling water reactor design and the design with an external gas-cooled reactor. However, the integrated gas-cooled reactor is mechanically complex and consequently it features a high investment cost.

6.3.6.6 Radial flow reactor

As in a boiling water reactor the radial flow reactor is cooled by circulating boiling water. However, in the radial flow reactor the catalyst is installed on the shell side and the boiling water flows on the tube side. The synthesis gas feed flow is distributed along the shell of the reactor and flows towards the centre where it is collected in a centre tube.

The benefit of a radial flow reactor is that higher single-line capacities may be achieved as the capacity can be increased by increasing the height of the reactor. I.e. the tube sheet diameter is no longer the constraint. From an efficiency point of view the radial flow reactor is an intermediate between the boiling water reactor and an adiabatic reactor.

6.3.6.7 Slurry phase reactor

The only alternative to the fixed-bed reactor type, which has been tested on a larger scale, is the slurry phase system, where finely divided methanol synthesis catalyst is suspended in inert oil [ALLAM et al. 1998]. The heat of reaction may either be removed in an external heat exchanger or by inserting a coil into the slurry reactor.

The slurry reactor features good temperature control. The main disadvantages are that a slip of the inert oil increases the cost of chemicals. In addition the larger reactor volume as the maximum catalyst loading is 50wt% slurry concentration and a high degree of back mixing, which lowers the achievable per pass conversion.

6.3.7 Condensing methanol

The major drawback of the conventional synthesis of methanol is the need for recycling in order to achieve a high conversion of the make-up gas. Recycling is dictated by the unfavourable gas phase thermodynamics at the temperature required by the methanol catalysts available. However, the limitations dictated by gas phase equilibrium may be overcome by condensing the methanol produced on the catalyst inside the reactor [HANSEN 1990].

The concept of condensing methanol has been demonstrated on a pilot scale and plans for the demonstration of the integrated technology based on ATR and condensing methanol have been announced [SØRENSEN et al. 2004].

6.4 Methanol purification [8]

Methanol purification consists of a number of distillation columns. The number of columns will depend on the desired quality of the methanol product and the requirements for energy integration at the specific product facility.

6.4.1 Low-grade methanol

Low-grade methanol has two main applications: fuel and feedstock for a downstream olefin plant. No official or internationally recognised specification exists for low-grade methanol. Thus, the quality of low-grade methanol can be anything between stabilised raw methanol and methanol from which water has been partially removed.

In case the product is stabilised raw methanol, the purification process simply consists of a stabiliser column in which dissolved gases and very light by-products are stripped off.

In case the water content of the raw methanol is too high, a concentration column must be added to the purification system. In the concentration column the methanol will be evaporated in order to withdraw the desired amount of water. All heavy by-products normally remain with the methanol product.

[8] Chapter 6.4 sources: figures after Dybkjær/Nørgaard/Perregaard (HTAS), 2005.

6.4.2 High-grade methanol

A chemical-grade AA methanol is >99.85wt% methanol. The main part of the methanol produced today is of grade AA or similar quality. The grade AA quality can be achieved in either a two-column or a three-column distillation layout.

6.4.2.1 Two-column distillation

A two-column distillation layout consists of a stabiliser and a concentration column. In the stabiliser column dissolved gases and very light by-products are stripped off. In the concentration column the stabilised methanol is separated into four streams: from the bottom of the column water is withdrawn, from a centre tray higher by-products are withdrawn, from the top just under a rectifying section the product methanol is withdrawn and from the top light by-products are purged.

6.4.2.2 Three-column distillation

A three-column distillation layout consists of a stabiliser and two concentration columns. One of the two concentration columns operates at slightly elevated pressure. This will enable the use of condensation duty of the high-pressure column as reboiler duty in the low-pressure concentration column. Hereby the separation duty utilised in the distillation section may be reduced by as much as 30% compared with a two-column layout. The layout is shown in **Figure 29**.

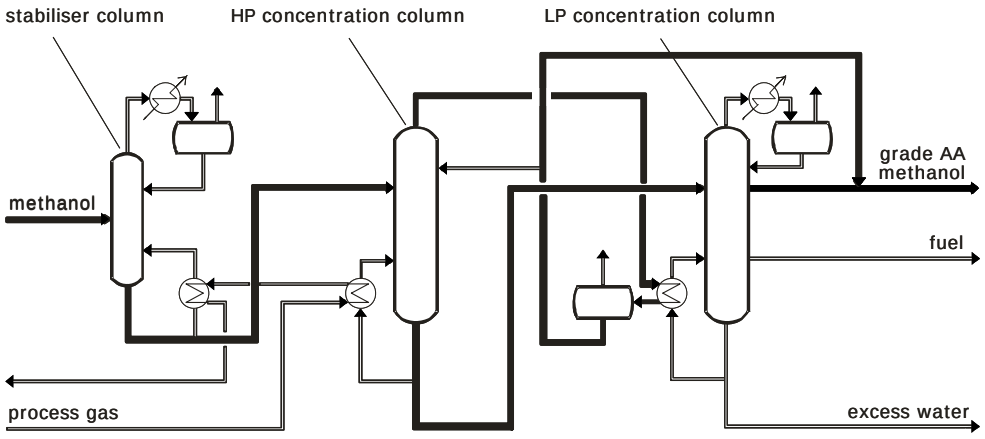


Figure 29: Methanol distillation with two concentration columns – simplified process flow diagram

6.5 Dimethyl ether technologies [9]

Dimethyl ether (DME) is the simplest aliphatic ether. It is a colourless gas at ambient conditions and has physical properties similar to LPG.

The total production of DME is in the order of 150,000 MTPY. It is today primarily used as a propellant. A large interest in DME as a clean fuel is giving grounds for optimism with respect to a potential very large growth in the market for DME. A number of applications are under consideration and are briefly listed below:

– LPG substitution,

– diesel fuel,

– fuel in power plants,

– hydrogen carrier,

– chemical intermediate (feed for MTO plants, synthetic gasoline, etc.).

If any of these applications materialise, a growth in DME consumption of many orders of magnitude can be foreseen. In **Table 17**, the application of DME today is given.

Table 17: Use of DME and market share

Use of DME	Market share
Hair spray	48%
Spray paints	6%
Insecticides	6%
Adhesives	5%
Industrial feedstock	31%
Miscellaneous	4%

Three routes for the production of DME dominate both the production and the literature on the subject:

– methanol/DME co-production,

– methanol dehydration,

– direct synthesis.

Until the late 1970s DME was obtained as a by-product of the high-temperature methanol technology used thus based on a co-production of methanol and DME. Today, the production is clearly dominated by the

[9] Chapter 6.5 sources: figures after Dybkjær/Nørgaard/Perregaard (HTAS), 2005.

methanol dehydration technology, whereas it is suggested in the open literature that their might be cost benefits by using a direct synthesis from synthesis gas in large-scale plants.

DME is formed via the dehydration reaction of two methanol molecules. I.e. methanol is also a precursor for the formation of DME in the direct synthesis. Consequently, the technology for the production of synthesis gas for DME production is identical to the synthesis gas technology for methanol production.

For the DME synthesis two distinct different designs are available. Either DME may be produced in a dedicated DME synthesis by dehydration of methanol. Upstream the dedicated DME synthesis a dedicated methanol synthesis is installed. Alternatively, the DME may be produced in a combined synthesis unit, in which the formation of methanol and DME takes place as parallel reaction in the same synthesis loop.

6.5.1 Methanol dehydration

The feedstock for a methanol dehydration unit is raw methanol as produced in a conventional methanol synthesis loop.

The methanol feed is evaporated and routed to the DME synthesis reactor, where the methanol is converted into DME. Per pass efficiencies of more than 80% may be achieved.

The DME synthesis reactor may either be an adiabatic fixed-bed reactor or a tube and shell type reactor where the heat of reaction may be removed by circulating oil. The DME synthesis typically operates at pressures ranging from 15–20 barg.

DME is separated in a distillation column. The bottom product consists of water formed in the dehydration reaction and unreacted methanol. Water can be separated from methanol in a waste water column, and unreacted methanol may be recycled to the synthesis reactor.

6.5.2 Combined synthesis

In a combined synthesis the synthesis of methanol and DME is performed in one synthesis loop ([DYBKJÆR et al. 1997], [SØRENSEN et al. 2003]). The feedstock to the combined synthesis loop is synthesis gas identical to the methanol synthesis gas as described above. The combined synthesis loop features a dual-function catalyst with activity for both the synthesis of methanol and the synthesis of DME. Thus, the product from the synthesis loop is a mixture of DME, methanol and water corresponding to the

equilibrium under the selected process conditions in the synthesis loop. To enhance the per pass conversion the synthesis loop will be designed to operate at high pressure, say 100 barg.

To further enhance the per pass conversion a refrigeration loop may be added to the process enabling chilling of the reactor effluent and further recovery of DME in the liquid phase leaving the loop as product. A simplified flowsheet of the combined synthesis is shown in **Figure 30.**

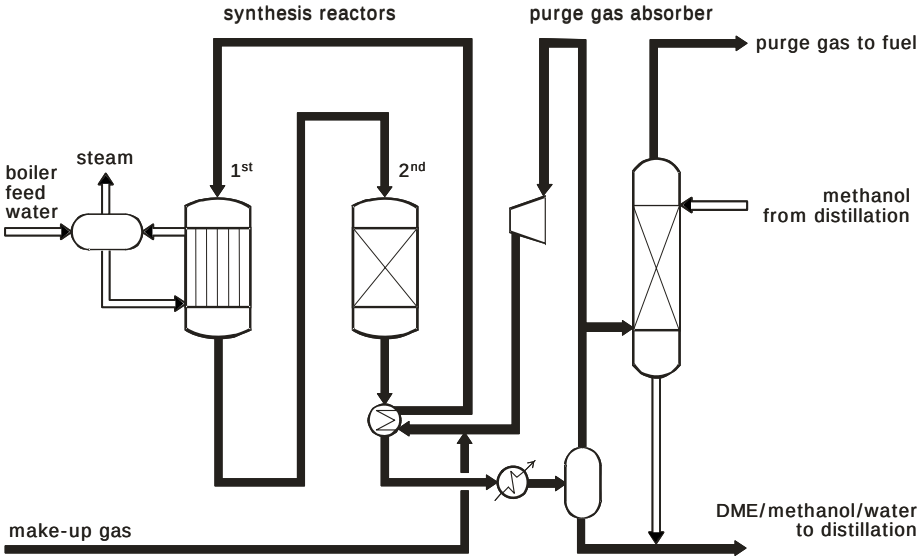


Figure 30: Combined synthesis of methanol and DME – simplified process flow diagram

6.5.3 Catalysts

In order to produce DME, an acid function in the catalyst is required. This statement is true both for the technologies based on the dehydration of methanol as well as the integrated synthesis technologies using a synthesis gas as feed. However, the strength and type of the acid catalytic site varies between the different suppliers/technologies. Both Brøndsted and Lewis acid sites are active, and the strength of the acid site is adjusted to ensure a sufficiently low tendency to coke formation to avoid rapid deactivation of the catalyst. For the integrated technologies a second function of the catalyst is required. The term dual-function catalyst is often used referring to a catalyst having both a methanol synthesis activity from synthesis gas and a dehydration function in the form of an acid function.

6.5.3.1 Dehydration catalysts

The reaction catalysed by the dehydration catalysts is:

$$2\ CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O \qquad (-\Delta H_{298K} = 23.4\ kJ/mol) \qquad \text{eq. 6.4}$$

Numerous catalysts have been suggested and include (but are not limited to) iron chloride, copper sulphate, aluminium chloride and aluminium phosphates. Industrially, the most important catalyst is based on aluminium oxide or aluminium silicates with or without promoters.

The reaction is generally very selective with the formation of only minor amounts of by-products like hydrocarbons. The key point for the catalyst is to have a sufficiently high acidity in order to have a high activity but without having a pronounced function of forming coke on the catalyst surface.

The mostly used kinetic models are based on the Langmuir-Hinshelwood mechanism and the rate-limiting step is considered to be the reaction between the two adsorbed methanol molecules.

6.5.3.2 Catalysts used in integrated technologies

Besides the dehydration reaction (eq. 6.4) the following reactions are also catalysed by the catalysts used in the integrated technologies:

$$CO_2 + 3\ H_2 \Leftrightarrow CH_3OH + H_2O \qquad (-\Delta H_{298K,\ 50bar} = 40.9\ kJ/mol) \qquad \text{eq. 6.1}$$

$$CO + 2\ H_2 \Leftrightarrow CH_3OH \qquad (-\Delta H_{298K,\ 50bar} = 90.7\ kJ/mol) \qquad \text{eq. 6.2}$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (-\Delta H_{298K,\ 50bar} = 49.8\ kJ/mol) \qquad \text{eq. 6.3}$$

The term ‘dual-function catalyst’ is often used. In the gas phase version of the integrated technologies a catalyst based on the traditional methanol synthesis system ($Cu/Zn/AL_2O_3$) is combined with an acid function. The acid function can be in the form of promoted alumina or a zeolite-based material. The *SAPO* type of materials (silicoaluminophosphate catalysts) has also been mentioned in the open literature.

In the slurry bed version of the technology more than one catalyst is often used. In this technology, catalyst powder is suspended in an appropriate fluid. Thus, it is easy to use a physical mixture of different materials. A traditional methanol catalyst powder combined with alumina or aluminium phosphates has been mentioned. A large effort by Air Products aimed at using molecular sieves as the catalyst resulted in the conclusion that it was not possible to find a material with a superior performance compared to the combination mentioned above.

6.6 Methanol reforming in water gas shift reactors [10]

The need for hydrogen will continue to increase especially in the refinery industry as the requirements concerning sulphur and aromatics content become more stringent due to environmental concerns and as the feedstocks become heavier (higher content of higher hydrocarbons) [ROSTRUP-NIELSEN 2002b]. Both methanol (MeOH) and dimethyl ether (DME) can be seen as convenient energy carriers as both chemicals can be easily steam reformed to generate hydrogen with a high yield.

A novel concept has been invented where the steam reforming of methanol or DME is carried out concurrently with the water gas shift reaction in the existing shift reactors in hydrogen plants. This concept represents an inexpensive and flexible option for debottlenecking hydrogen production capacity in existing hydrogen plants.

6.6.1 Thermodynamics

When using methanol as co-feed to a shift reactor it is instructive to consider the thermodynamics of the two reactions

$$CO + H_2O = CO_2 + H_2 \qquad -\Delta H^{shift}_{280°C} = 37.83\ kJ/mol \qquad \text{eq. 6.5}$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad -\Delta H^{MeOH,reform}_{280°C} = -63.01\ kJ/mol \qquad \text{eq. 6.6}$$

The shift reaction is mildly exothermic whereas methanol steam reforming is moderately endothermic. It can be seen that at 280 ºC

$$\Delta H^{MeOH,reform}_{280C} = 5/3 \times (-\Delta H^{shift}_{280°C}) \qquad \text{eq. 6.7}$$

It is thus possible to reform 3 moles of methanol per every 5 moles of CO shifted under isothermal conditions by using the reaction heat of the shift reaction to drive the methanol reforming reaction. This means that an additional 9 moles of hydrogen is generated per 5 moles of CO converted in the shift reactor.

The principle can also be used if DME is introduced to the shift reactor because DME can be converted to methanol according to:

$$CH_3OCH_3 + H_2O = 2\,CH_3OH \qquad -\Delta H^{DME,hydration}_{280°C} = -21.71\ kJ/mol \qquad \text{eq. 6.8}$$

[10] Chapter 6.6 sources: figures after [HANSEN et al. 2005].

This will require an additional solid acid catalyst function, whereas methanol reforming and shift can be performed simply using a modified copper-based catalyst.

6.6.2 The kinetics of methanol reforming in low-temperature water gas shift reactors

The kinetics of the industrial low-temperature water gas shift reaction and methanol synthesis reaction have previously been studied extensively and microkinetic models have been proposed for both reactions ([OVESEN et al. 1996], [OVESEN et al. 1997]). The active site for both reactions has been proposed to be metallic copper. This hypothesis has been substantiated by a vast number of in-situ experiments including EXAFS and TEM studies ([CLAUSEN et al. 1991], [HANSEN et al. 2002]). The microkinetic model has been able to describe the reaction rate for the water gas shift reaction measured over the commercial low-temperature catalyst and the reaction rate of methanol synthesis measured over the commercial methanol catalyst. The understanding of the kinetics of methanol reforming in low-temperature water gas shift reactors can be based on these models.

A simplified kinetic model can be developed based on the microkinetic model. A simulation with the full microkinetic model shows that the surface species present in large amounts under water gas shift conditions are hydrogen and formate. The simplified kinetic model is:

$$r_{reforming} = k_{reforming} \frac{P_{CH_3OH}\, P_{H_2O}}{P_{H_2}^{1.5}\, P_0^{0.5}} (1-\beta) \cdot \theta_*^{2}$$

$$r_{shift} = k_{shift} \frac{P_{CO}\, P_{H_2O}}{P_{H_2}\, P_0} (1-\beta) \cdot \theta_*^{2}$$

$$\theta_*^{-1} = 1 + K_{H_2} \left(\frac{P_{H_2}}{P_0} \right)^{0.5} + K_{HCOO*} \frac{P_{CO_2}\, P_{H_2}^{0.5}}{P_0^{1.5}}$$

Here P_0 is the reference pressure 1 atm. The pre-exponential factors for the rate constant of methanol reforming and water gas shift have been adjusted to fit experimental measured rates of methanol reforming and shift reaction under methanol to shift conditions. The activation barrier for methanol reforming and water-gas shift is taken from the microkinetic model [OVESEN et al. 1997]. In addition, the adsorption constant of hydrogen and formate is taken from the microkinetic model [OVESEN et al.

1997]. The kinetic model is an important tool for designing the methanol to shift reactor and determining the optimal operation condition. It is important to strike the right balance between the shift reaction and methanol reforming reaction in order not to reach too high temperatures, which could be detrimental to the catalyst, or too low temperatures, which could lead to incomplete methanol conversion. One example is shown in **Figure 31**.

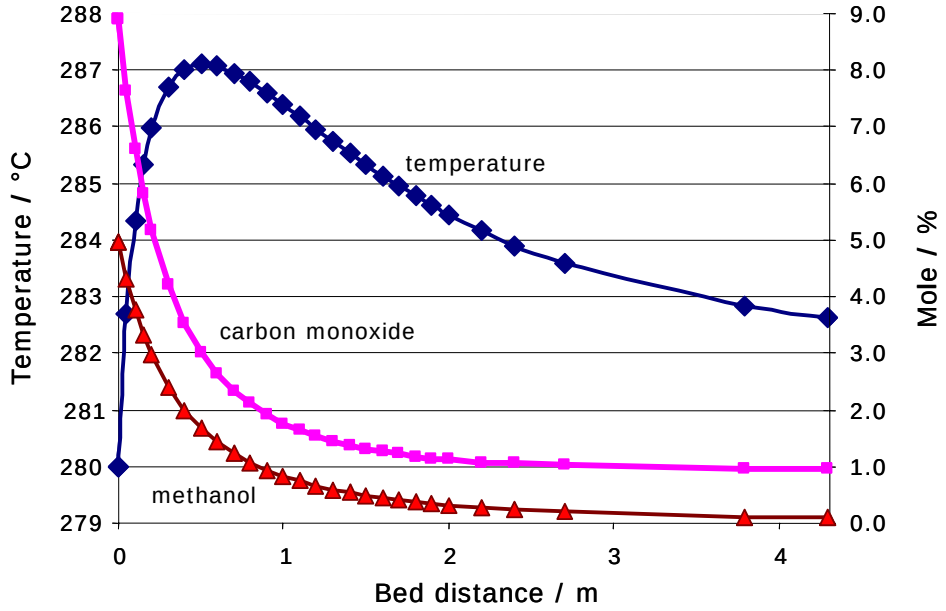


Figure 31: Temperature, CO and methanol profiles in shift reactor

It can be seen that both reactions are carried out close to the optimum temperature/conversion path and there is thus ample catalyst volume available in the existing reactor to achieve conversion to equilibrium for both reactions.

6.6.3 Industrial applications

Revamp of an existing hydrogen plant by incorporating a Methanol-to-Shift™ is quite simple as shown below in **Figure 32**.

From a large methanol storage tank away from the hydrogen plant methanol is delivered to a day tank from which it is pumped to operating pressure and evaporated in a steam-heated evaporator and then sent in the vapour form to an existing shift reactor with the Haldor Topsøe catalyst LK-510.

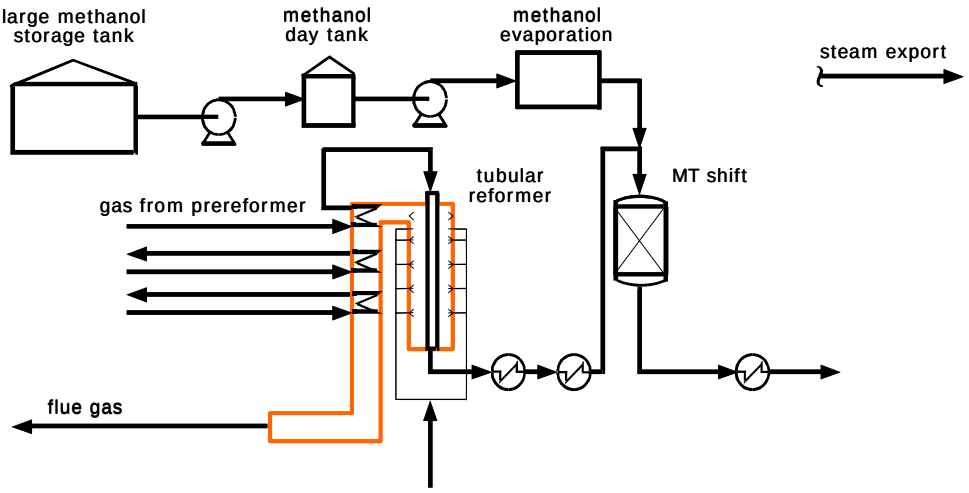


Figure 32: Revamp of hydrogen plant by Methanol-to-Shift™

The only additional major part of the hydrogen plant needing revamp would normally be the pressure swing adsorption (PSA) unit, which has become the standard for final hydrogen purification. The duties in the primary reformer remain essentially unchanged but the steam to carbon ratio can be slightly increased in order to maintain a reasonable plant fuel balance.

Table 18: Operating conditions before and after revamp by installation of Methanol-to-Shift™

Operating conditions	Before revamp	After revamp
H_2 production / (Nm^3/h)	49,000	61,250
Natural gas / (Nm^3/h)	18,575	18,956
Methanol / (kg/h)	-	6,578
Steam export / (MT/h) @(~45 bar, 400ºC)	35.4	24.7
$T_{IN/OUT,\ shift\ converter}$ /°C	210/330	272/292

The plant operating conditions before and after the revamp of a typical modern hydrogen plant are shown in **Table 18**. The revamp can be carried out with short project duration and a minimum of downtime due to the relatively simple modifications involved ([MADSEN DYBKJÆR 2004], [HANSEN et al. 2005]).

6.6.4 Economic considerations

Using in-house cost data it has been estimated by Haldor Topsøe that the investment in a Methanol-to-Shift™ revamp is 40% of the investment in a new plant.

The changes in total production and consumption figures are shown in **Table 19** for the two options.

Table 19: Changes in total production and consumption figures

Production, consumption	Methanol-to-Shift™ revamp	New plant
H_2 production / (Nm^3/h)	+12,250	+12,250
Natural gas cons. / (Nm^3/h)	n.a.	+4,708
Methanol cons. / (kg/h)	6,578	n.a.
Steam export / (MT/h)	-7.6	+8.4

n.a. = not available

The optimum choice obviously very much depends on the price of natural gas and methanol and the value put on the steam as well on ROI required for the capital invested. Using the default values of 3.8 €/GJ_{LHV} for natural gas, 100 €/MT for methanol and a steam value of 12 €/MT the two options are found to give the same production cost of around 70 € per 1,000 Nm^3_{H2} produced.

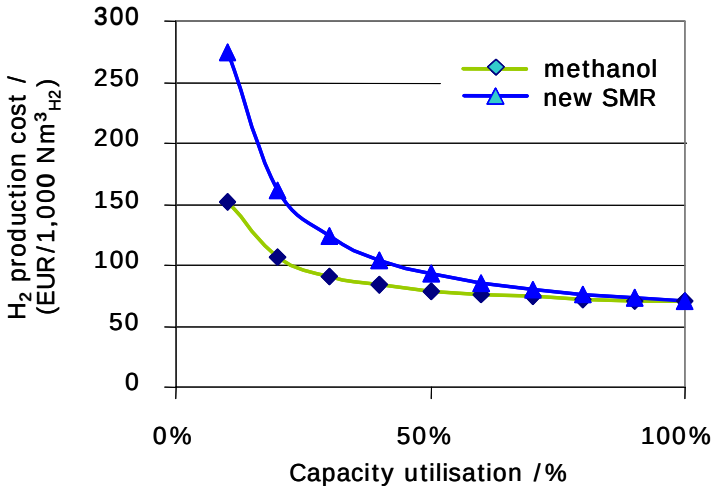


Figure 33: Effect of capacity utilisation

This analysis, however, ignores the benefits of Methanol-to-Shift™ with respect to a very short implementation time and quick response to load change in the plant. Especially for peak shaving purposes Methanol-to-Shift™ is attractive as illustrated in **Figure 33** comparing the production cost for the two options.

6.6.5 Conclusions

Revamping of hydrogen plants by introducing methanol to an existing shift reactor offers the possibility of increasing the total plant output by more than 30% with a relatively modest investment and very short implementation times. The concept is especially suited for peak shaving operation where the normal feedstock is relatively expensive.

Because both the shift and methanol reforming reactions are carried out close to the optimum temperature/conversion path under almost isothermal conditions there is ample activity available using copper-based catalysts.

This new process offers the possibility of using methanol (or DME) produced from a variety of raw materials as a hydrogen carrier.

6.7 Use of methanol and DME in solid oxide fuel cell systems [11]

6.7.1 Introduction

Methanol (MeOH) (and dimethyl ether, DME) could be attractive fuels for use in SOFC combined heat and power plants. Potentially, the fuel processing steps in the plant could be very simple: ultimately being only evaporation of the methanol and injection into the anode chamber of the SOFC.

This approach would, however, lead to a number of problems and disadvantages:

- Dry MeOH (and DME) is prone to form carbon under conditions prevailing in the anode chamber even with the most active Ni-cermets as the anode material as described in [SOUNDERS et al. 2004]. The amount of water needed to avoid carbon formation is calculated in [SASAKI TERAOKA 2003].

[11] Chapter 6.7 sources: figures after [HANSEN et al. 2005].

- Compared to a natural-gas-based system, more parasitic losses would be incurred for cathode air compression and the cathode air in/out exchanger would become considerably larger for a MeOH- or DME-based system. This is due to the fact that the cathode air is used for cooling the stack and that internal reforming of methane in the anode chamber, in the case of natural gas feed, helps to cool the stack due to the endothermal nature of methane steam reforming. The heat of reactions for reforming methanol or DME is much less endothermic than methane steam reforming.

A process layout where all these problems are overcome has been developed by adiabatically converting MeOH or DME into a mixture of methane, CO, CO_2 and water. In this way, part of the chemical energy contained in the feedstock is converted to a temperature increase across the methanator thereby eliminating the need for an anode in/out heat exchanger and converting MeOH and DME into methane, which is much less prone to carbon lay down than CO which could be formed from the feedstock. At the same time the chemical energy converted into latent heat in the methanator does no have to be removed by excess cathode air in the SOFC, thus increasing overall electric efficiency of the system.

An anode recycle stream can conveniently be included by means of an ejector upstream the methanator using as motive force methanol compressed by a pump and evaporated using waste heat from the system. For DME the pump is superfluous as the DME will have a sufficient vapour pressure under ambient conditions to drive the ejector recycle.

6.7.2 Methanol-based SOFC systems with methanol methanation

Based on these considerations a system with methanol as the feed and an ejector recycle of anode off-gas to the MeOH methanator inlet has been designed and is depicted in **Figure 34**.

In one example of the process scheme, methanol is compressed by means of pump **P 1** and evaporated in **E 1** by means of waste heat in the flue gas from the catalytic burner. The gas leaving **E 1** acts as the motive force in ejector **X 1**, whereby part of the anode off-gas is recycled back to the MeOH methanator, **R 1**, which is loaded with a catalyst active for methanol decomposition and methanation. The gas is sent directly from the methanator to the SOFC stack.

Air is compressed in **K 1** and preheated to the cathode inlet temperature in **E 3**. Part of the cooled cathode off-gas from **E 3** is burned with anode gas not recycled to **R 1** in the catalytic burner. The rest of the air supplies waste heat for heating application in heat exchanger **E 7**. The flue gas delivers heat for methanol evaporation in **E 1** and delivers waste heat for heating in **E 5**.

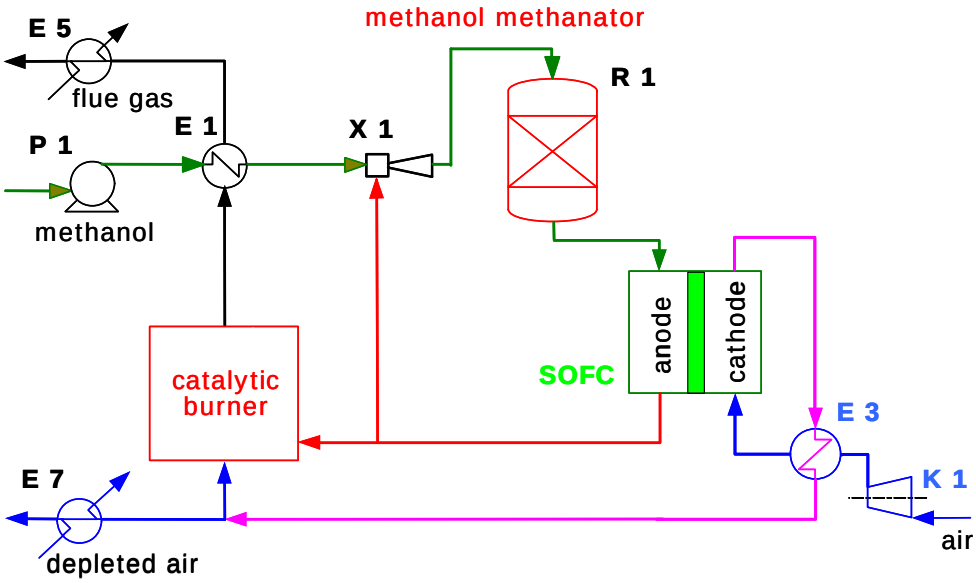


Figure 34: Process scheme of a MeOH-based SOFC systems with MeOH methanation

The MeOH methanation concept has the following benefits compared to direct MeOH injection to the SOFC stack:

- eliminates potential carbon formation problems,
- eliminates the need for an anode in/out heat exchanger,
- increases the electric efficiency by 2% relative,
- reduces the combined heat exchanger duties,
- reduces air compressor work.

The disadvantages are only an investment in a small methanol methanation reactor.

Almost the same benefits can be obtained when using DME as the feedstock and methanate it before the SOFC stack. A small advantage with DME compared to methanol is that the fuel pump can be omitted.

6.8 Summary of Chapter 6

Commercially used methanol technologies need three process units and a utility section: synthesis gas preparation (reforming), methanol synthesis, methanol purification and utilities. In the synthesis gas preparation section, the hydrocarbon feedstock is purified of for instance sulphur before being converted into synthesis gas at high temperature and subsequently compressed to synthesis pressure. Several reforming technologies are available for the gas conversion: one-step reforming with a tubular reformer, two-step reforming, autothermal reforming (ATR).

In the methanol synthesis section, the synthesis gas is converted to raw methanol, which contains water and minor amounts of by-products. The straight-tubed boiling water reactor is often used being the most efficient reactor type. Water and by-products are removed in the methanol distillation section. The conventional layout is with a two-column system. The Topsøe system features a split concentration column and an optional ethanol column. The utility section comprises water treatment, cooling water system, auxiliary boiler, power production, and other installations as required for the proper operation of the plant. Typical capacities for world-scale methanol plants have been in the range of 1,500–2,500 MTPD. Lately, the trend has been to obtain lower production costs by building even larger plants to achieve economy of scale.

DME as a clean fuel is very interesting for the market. Possible applications are LPG substitution, diesel fuel, fuel in power plants, hydrogen carrier and chemical intermediate (feed for MTO plants, synthetic gasoline, etc.). Three routes for the production of DME dominate both the production and the literature on the subject: methanol/DME co-production, methanol dehydration and direct synthesis.

Both methanol (MeOH) and dimethyl ether (DME) can be seen as convenient energy carriers as both chemicals can be easily steam reformed to generate hydrogen with a high yield. A novel concept has been invented where the steam reforming of methanol or DME is carried out concurrently with the water gas shift reaction in the existing shift reactors in hydrogen plants. Revamping of hydrogen plants by introducing methanol to an existing shift reactor offers the possibility of increasing the total plant output with a relatively modest investment and very short implementation times. This new process offers the possibility of using methanol (or DME) produced from a variety of raw materials as a hydrogen carrier.

7 Methanol technologies [12]

After having described the conventional technology for methanol production (**Chapter 4**), future-oriented methanol technologies will be presented in the following. A compilation of different Lurgi processes can be found in **Table 35**.

7.1 Natural gas-to-methanol

The *MegaMethanol®* process is a future-oriented technology for the conversion of natural gas into methanol in large quantities and at low cost. This technology enables the construction of single-line plants with high efficiency and more than twice the production capacity of today's methanol plants. This permits the use of methanol in new downstream processes (DME, polypropylene).

7.1.1 The concept

The *MegaMethanol®* technology was developed for large plants with a capacity of > 1 million t/y (3,000 t/d) of methanol. In order to achieve such capacities, a special process design is needed, which is based on a modern but proven and reliable technology, a cost-optimized energy use, high environmental compatibility and low investment costs [GÖHNA 1997].

The essential features of this technology are:

– autothermal natural gas reforming with oxygen supply in combination with steam reforming or as pure autothermal reforming,
– two-stage methanol synthesis with water- and gas-cooled reactors enabling operation under optimum reaction conditions,
– adjustable synthesis gas composition by the mode of operation of the hydrogen loop.

7.1.2 Synthesis gas production

The costs for the production unit of the synthesis gas account for approximately 50% of the investment costs of a methanol plant. The optimisation of this plant component therefore holds the greatest potential for cost savings.

[12] Chapter 7 is based on: Bielawa in [METHANOL 2003], Chapter 5. Updated by Liebner

Pure conventional steam reforming is only economically efficient in small and medium-sized methanol plants and technically limited to a maximum capacity of about 3,000 t/d of methanol for single-strand plants. Oxygen-based natural gas reforming, both in combination with steam reforming and as pure autothermal reforming, is regarded today as the best concept for large synthesis gas plants [CHRISTENSEN PRIMDAHL 1994].

The configuration of the reforming process (cf. **eq. 4.1** in **Chapter 4.1.1**) essentially depends on the composition of the feedstock, which may range from light natural gas (nearly 100% methane content) up to associated gas. The aim of the reforming process is in all cases the production of an optimum synthesis gas for methanol production (cf. **eq. 4.2** in **Chapter 4.1.2**), which is characterized by the stoichiometric number S_R[13] defined in the following: $S_R = (H_2\text{-}CO_2) / (CO+CO_2) = 2.0–2.1$.

7.1.3 Autothermal reforming

Pure autothermal reforming can be used for synthesis gas production whenever light natural gas is available as a feedstock.

The desulphurized and (optionally) prereformed natural gas is reformed with steam and oxygen as the reforming agent at about 40 bars to obtain synthesis gas. The process provides great flexibility, so that operation can be adapted to the specific requirements over large ranges. The reformer outlet temperatures are in the range of 950–1,050 °C. The synthesis gas is compressed to the pressure required for methanol synthesis in a synthesis gas compressor with integrated recycle stage.

Even if pure methane is used as the feedstock for autothermal reforming, it is necessary to condition the synthesis gas since the stoichiometric number is smaller than 2.0. The most effective way to achieve the gas composition required is the addition of hydrogen, which is obtained from a purge gas flow of methanol synthesis by means of a membrane assembly or a pressure swing adsorption unit (PSA).

7.1.4 Combined reforming

In the case of using heavy natural gases and associated gas, the stoichiometric number required cannot be achieved, even if all the hydrogen available in the purge gas is fed to the synthesis gas. In these cases, the *MegaMethanol®* concept provides for a combination of autothermal and

[13] S_R is equal to the module M (cf. **Chapter 5.2.2, 5.3.1 and 6.2.3**)

steam reforming *(Combined Reforming)* to produce the synthesis gas for methanol plants in the most economical manner (**Figure 35**).

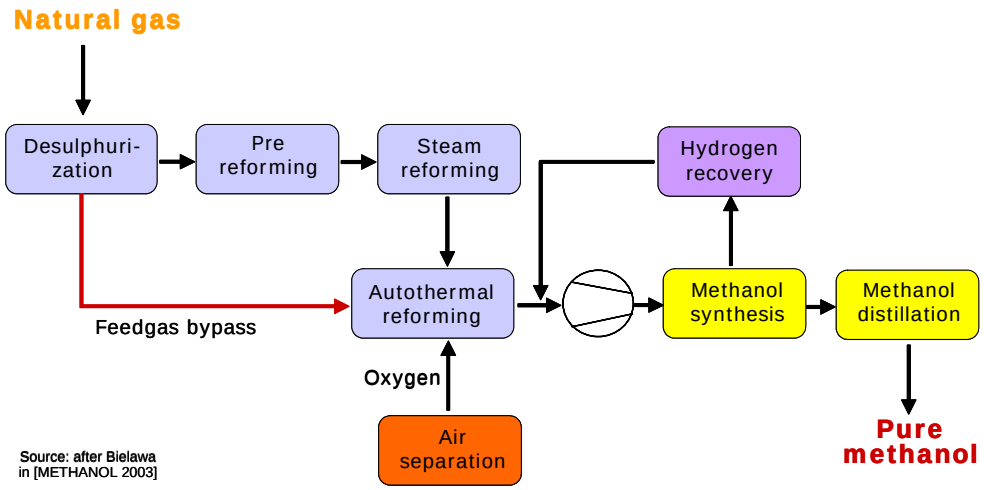


Figure 35: Methanol production by *Combined Reforming* [HAID 2001a]

Following desulphurization, a partial flow of the natural gas is converted in a steam reformer at high pressures (35–40 bars) and comparatively low temperatures (700–800 °C). The reformed gas is then combined with the remaining desulphurized natural gas and reformed to synthesis gas in the autothermal reformer at high pressure. This concept is designated *Combined Reforming*.

The essential advantage of *Combined Reforming* over comparable process alternatives is the patented natural gas bypass around the steam reformer. In the case of most natural gases, less than half the natural gas is passed through the steam reformer. The total process steam requirement is also only half that of other processes, in which an autothermal reformer is arranged behind a steam reformer without such a bypass. This lower consumption of process steam results in lower energy requirements and lower investment costs.

The *Combined Reforming* process is also ideal for the production of synthesis gas for Fischer-Tropsch synthesis. The world's largest plant of this type was built by LURGI in South Africa. The synthesis gas capacity of this plant is sufficient for the production of more than 9,000 t/d of methanol.

7.1.5 Methanol production

An effective conversion of synthesis gas into methanol is essential for low-cost methanol production. In addition, the optimum utilization of the process heat provides cost benefits and energy saving potentials for the entire plant. LURGI has already equipped its methanol plants with a tubular reactor transferring the reaction heat to boiling water since the entry of low-pressure methanol technology [GÖHNA 1997].

This methanol reactor is in principle a vertical tube-bundle heat exchanger with fixed tube sheet. The catalyst is contained in the tubes and rests on an inert material bed. The boiling water/steam mixture produced by the reaction heat is extracted below the upper tube plate. The reaction temperature can be exactly controlled by regulating the steam pressure. This isothermal reactor achieves very high yields at a low recycle ratio (the ratio of fresh gas to recycle gas) and minimizes the formation of byproducts.

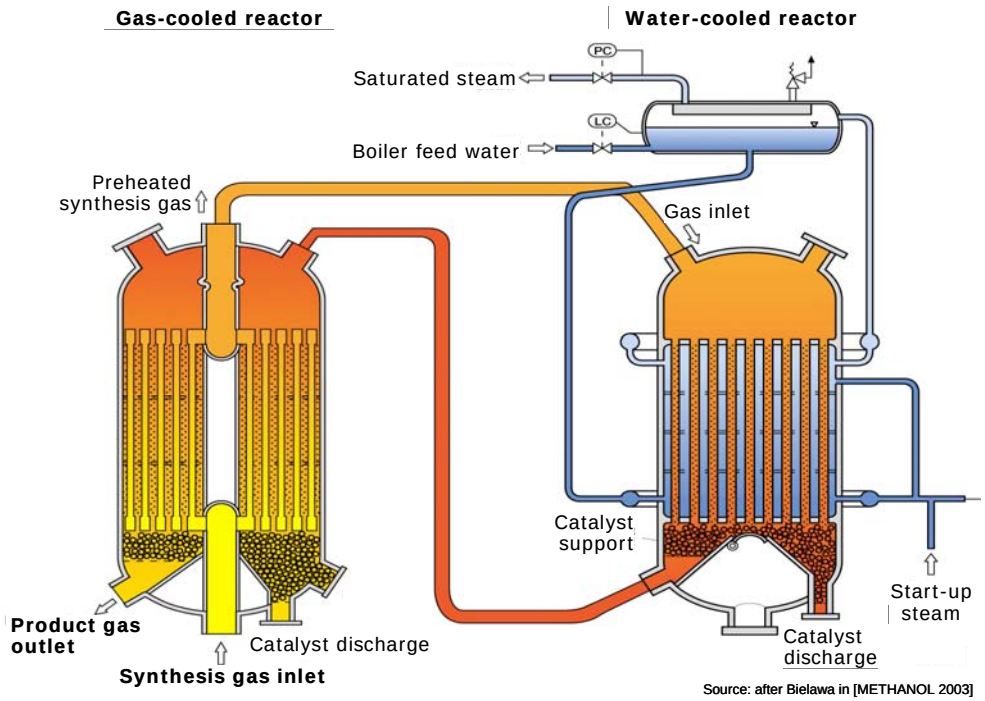


Figure 36: Two-stage methanol synthesis using the MegaMethanol® process [LURGI 2003]

Based on this methanol reactor and the highly active methanol catalyst [RINGER 2000], which in combination permit high space velocities, LURGI has recently developed a two-reactor system with high efficiency (**Figure 36**), in which the isothermal reactor is connected in series with a gas-cooled reactor.

In the first, isothermal, water-cooled reactor, a partial conversion of the synthesis gas into methanol is achieved at higher space velocities and higher temperatures than in reactors of single-stage methanol synthesis. This leads to a significant reduction in size of the water-cooled reactor in comparison to conventional processes, whereas the steam produced is obtained at a higher pressure and thus energy level.

The methanol-containing gas, which leaves the first reactor, is passed without prior cooling through a second gas-cooled reactor installed behind. In this reactor, the cold inlet gas for the first reactor is passed through tubes in counterflow to the reaction gas. The reaction temperature along the reaction path is thus continuously lowered in the second reactor and the driving force of the reaction equilibrium maintained throughout the catalyst bed (**Figure 37**).

Fresh synthesis gas is only fed to the first reactor, so that no catalyst poisons can reach the second reactor. The operation with high-purity inlet gas and the low operating temperature lead to an almost unlimited service life of the catalyst in the gas-cooled reactor.

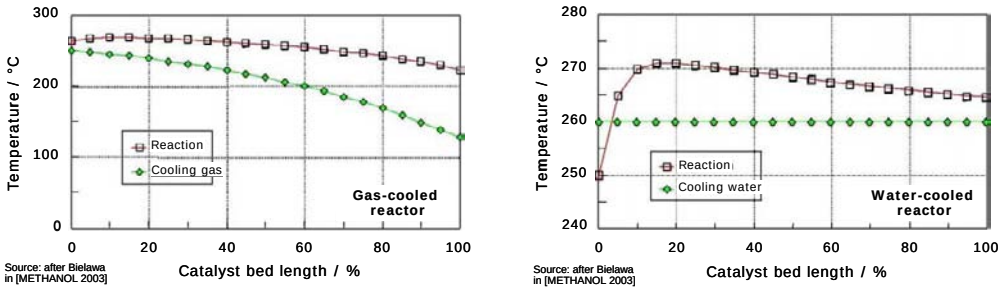
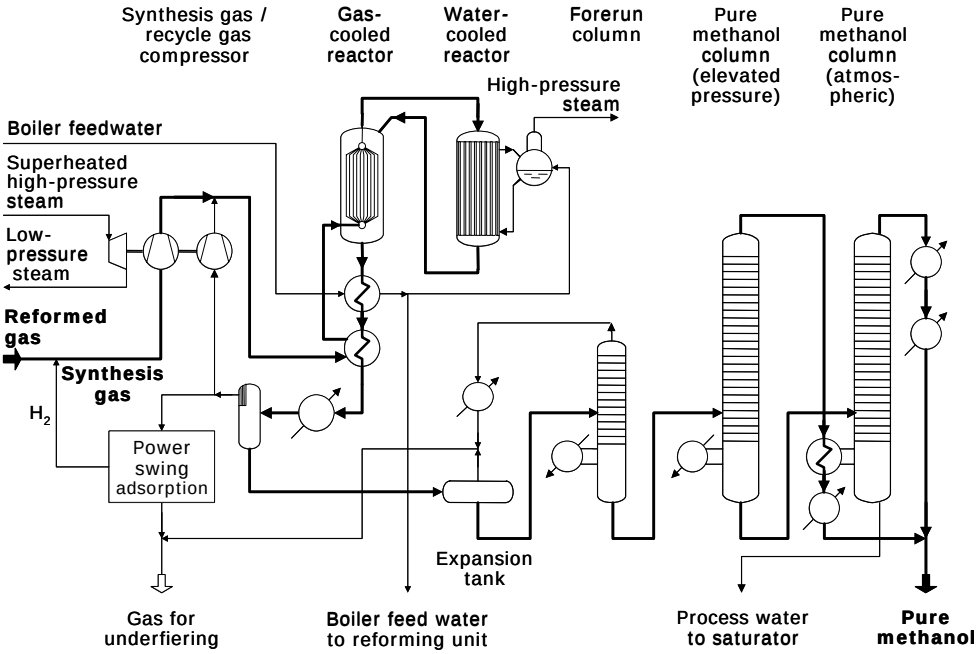


Figure 37: Temperature profiles of two-stage methanol synthesis using the MegaMethanol® process [LURGI 2001]

Moreover, the service life of the catalyst in the water-cooled reactor is also prolonged due to the optimized reaction process in the two-stage methanol synthesis *(combined converter methanol synthesis)*. If the methanol yield in the water-cooled reactor decreases due to reduced catalyst activity, the temperature in the inlet zone of the gas-cooled reactor

will rise, which improves the reaction kinetics and thus increases the methanol yield in the second reactor.

After cooling the reaction mixture and separating the crude methanol from the non-converted reaction gas, the crude methanol is processed in the distillation unit. In the hydrogen recovery unit, hydrogen is separated from a purge gas partial flow and recycled into the synthesis gas loop. The remaining methane-rich gas is used for underfiring.



Source: after Bielawa in [METHANOL 2003]

Figure 38: Two-stage methanol synthesis with 3-column distillation [GÖHNA 1997]

The essential advantages of the two-stage methanol synthesis (**Figure 38**) are:

– High efficiency of synthesis gas conversion: at the same rate of conversion, the recycle ratio (fresh gas/recycle gas) is only about half as high as in a single-stage water-cooled reactor.

– High energy efficiency: about 0.8 t of steam per ton of methanol can be produced at 50–60 bars. Moreover, a considerable proportion of the free heat at the outlet of the gas-cooled reactor can be recovered.

– Low investment costs: due to the reduction of the catalyst volume for the water-cooled reactor, the omission of the large inlet gas preheater

and the savings for other equipment parts owing to the lower recycle ratio, specific savings of about 40% are achieved for the synthesis loop.

– High single-line capacity: single-line plants with a capacity equalling 5,000 t/d of methanol and more can be built using the *MegaMethanol*® technology.

7.1.6 Methanol distillation

The crude methanol is cleaned up in an energy-saving distillation unit composed of three columns.

In the 3-column configuration, the low boilers are separated in a prerun column and the high boilers in two pure methanol columns. The first pure methanol column is operated at elevated pressure, whereas the second runs at almost atmospheric pressure. The overhead vapours of the pressure column heat the bottom of the atmospheric column. In this way, about 40% heating steam as well as 40% cooling capacity is saved. The separation into two pure-methanol columns also permits the construction of very high single-line capacities.

7.1.7 Evaluation of economic efficiency

Raw material costs and capital costs are the essential parameters of the production costs.

Table 20: Economic efficiency of steam reforming plants

Characteristics	Conventional steam reforming	*MegaMethanol*®
Capacity / ($t_{methanol}$/d)	2,500	5,000
Natural gas consumption (based on LHV) / (MMBtu/t)	30	28.5
Capex / % *Opex* / % Production costs / %	100 100 100	140 97 79

Capex = capital expenditure; *Opex = operational expenditure*

Table 20 shows a comparison between the *MegaMethanol*® process and a conventional steam reforming plant with respect to raw material consumption, capital input and resulting production costs. The results show that the

high economic efficiency of the process and the low investment costs of a *MegaMethanol®* plant permit a clear reduction of methanol costs.

The resulting stable and low methanol price in the long term paves the way for a broader use of methanol both in the energy sector and as a feedstock in petrochemistry [STREB GÖHNA 2000].

7.2 Dimethyl ether

Dimethyl ether (DME) has outstanding diesel properties (cetane number 55–60, zero sulphur and aromatics fraction; cf. **Table 21**; lower heating values cf. **Table 38**) and thus represents a future alternative to conventional diesel fuel for mobile applications. It is also regarded as an environment-friendly alternative to diesel in electric power generation *(MTPower®)* [LURGI 2003].

Table 21: Comparison of DME and diesel fuel [LURGI 2002]

Characteristics	DME	Diesel
Liquid density (@ 20 °C) / (kg/m^3)	666.0	< 845.0
Cetane number	55–60	40–55
Lower heating value LHV / (GJ/t)	28.84	~ 42.5
Sulphur content / (vol%) Aromatics content / (vol%)	0 0	~ 1.0 ~ 30.0

Table 22: Comparison of DME and LPG [LURGI 2002]

Characteristics	DME	LPG
Steam pressure (@ 20 °C) / (kPa)	530.0	520.0
Liquid density (@ 20 °C) / (kg/m^3)	666.0	540.0
Relative gas density (air = 1)	1.59	1.50
Normal boiling temperature (@ 0.1 kPa) / °C	-24.8	-42.1
Lower heating value LHV / (GJ/t)	28.84	46.0
"Bottle fill" * / %	85.0	80.0
Mass per filling volume / (kg/m^3)	567.0	432.0
Energy content per filling volume / (GJ/m^3)	16.3	19.9

* Degree of storage tank / bottle filling

Due to the similarity of its physical properties to those of LPG (liquefied petroleum gas) it can easily replace or complement LPG (especially with respect to storage and transport; cf. **Table 22**). In the concept for electric power generation with methanol and/or DME, methanol is produced with low-cost natural gas. Electric power generation then takes place at locations that have no natural gas supply through pipelines or LNG.

7.2.1 Production process

In order to obtain an economical fuel price, the DME must be produced in large-tonnage plants ("megatechnologies"). Traditionally, DME was a by-product in high-pressure methanol synthesis. After the development of low-pressure methanol synthesis, DME was produced by dehydration (elimination of water) in the presence of suitable catalysts. This process is carried out in fixed-bed reactors, the product is cooled and distilled to pure DME (**Figure 39**).

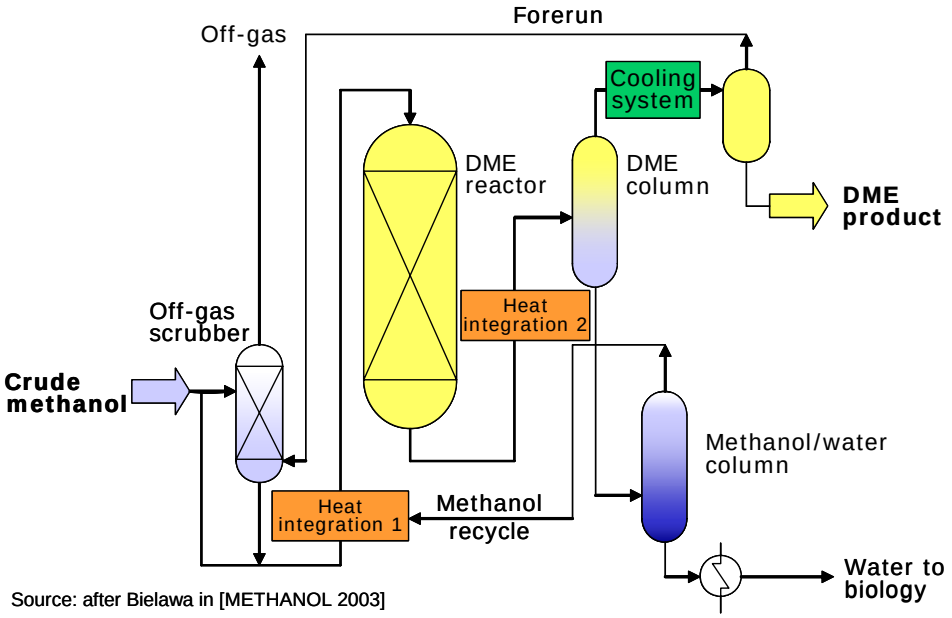


Figure 39: DME production from crude methanol [LURGI 2002]

A modification of methanol synthesis would permit the production of DME in the methanol synthesis loop as a byproduct with higher yields. However, this reaction pathway has two major disadvantages. The steam content rises during dehydration and thus enhances the water-gas shift reac-

tion. The quality of the synthesis gas deteriorates due to the conversion of CO into CO_2. The kinetics of the reaction of CO_2 and H_2 is slower than that of CO and H_2. Consequently, the synthesis catalyst and the recycle volume must be increased. In addition, a low-temperature separation of the DME is required due to its low boiling point [BALTHASAR HILSEBEIN 2003].

In the case of combining a DME unit with a *MegaMethanol®* plant it is possible to reduce the methanol distillation unit from a 3-column configuration to a single-column system, which involves corresponding savings.

In the *MegaDME* process (methanol-to-DME, *MTD*) all types and grades of DME can be produced. The different requirements for fuels, electric power generation *(MTPower®)* or pure DME can be met by varying the size and design of the DME distillation columns.

7.2.2 Evaluation of economic efficiency

The economic efficiency of the *MegaDME* process is summarized in **Table 23**, making the following assumptions:

– natural gas consumption and product value are normalized to one methanol equivalent (capacity: 7,500 t/d of methanol),
– the DME product quality corresponds to the given specifications,
– natural gas consumption figures comprise the energy requirement for an air separation and an electricity production unit,
– total fixed costs comprise an air separation unit, an electricity production unit and utility units,
– the natural gas price was assumed to be 1.0 US$/MMBtu,
– depreciation was assumed to be 10% of the total fixed costs,

Table 23: Economic efficiency of the *MegaDME* process [LURGI 2003]

Characteristics and costs		MegaMethanol® & dehydration
DME capacity / (t/d)		5,000
Specific natural gas consumption	/ (MMBtu/$t_{methanol}$)	28.5
	/ (MMBtu/t_{DME})	40.2
Total fixed costs (EPC [1]) / (million US$)		750 [2]
DME production costs / (US$ / t_{DME})		152 [2]

[1] engineering, procurement and construction; [2] extrapolated 2003 —> 2006

– the ROI (return on investment) was fixed at 20% of the total fixed costs,
– operating costs for plant, personnel, plant overhead costs, servicing/maintenance work and material are included.

The investment costs are budget cost estimates with an accuracy of ±30%, specific site factors are not included in these figures.

DME, a traditional methanol derivative, thus represents a promising alternative fuel to diesel, LPG, for electricity production and also for olefin production if produced in large quantities. DME production by dehydrating methanol is a more economical approach than the simultaneous production of methanol and DME. **Figure 40** shows a price comparison for DME with diesel fuel and LPG as of 2002/2003 and **Table 24** the same for 2006.

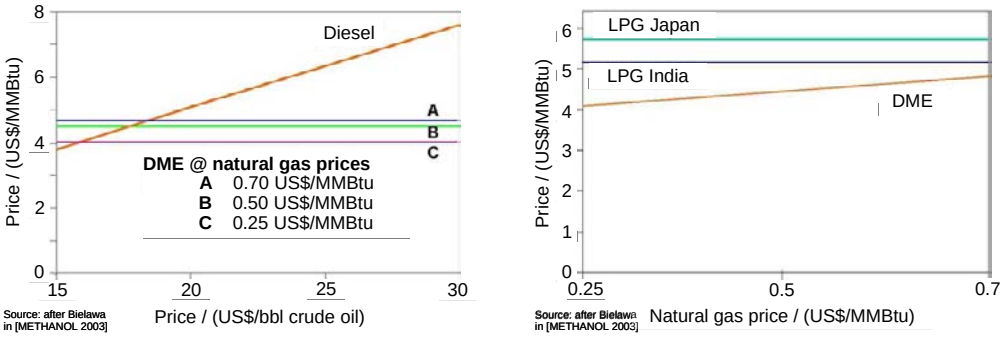


Figure 40: Comparison of DME with diesel and LPG ([LIEBNER 2002] LPG prices [CHEMSYSTEMS 2003])

Table 24: DME compared with diesel and LPG 2006 [LIEBNER 2006]

Fuel		Costs / ($/MMBtu)
DME	Production cost	5–7 [1]
	Transportation cost	0.5–1 [1]
	Delivered cost (“trans-ocean”)	6–8 [1]
Diesel		14 [1] [2]
LPG		11.4 [1] [2]

[1] Based on natural gas price = 1 US$/MMBtu and both depreciation & ROI 10% of total fixed costs; [2] as of March 2006

7.3 Methanol-to-hydrogen

The demand for hydrogen will in future be decisively determined by the hydrogen demand in refineries, especially since refineries are also subject to increasingly stringent environmental regulations while, at the same time, more and more wells with oil of poorer quality are being tapped. This additional demand will probably require almost a doubling of the installed hydrogen production capacity for use in refineries by 2005 in comparison to 1997 [HAID 2001b].

The preferred technology for hydrogen production will be the steam reforming of natural gas. In regions in which no natural gas is available, naphtha is currently used as an alternative feedstock in the steam reforming process. Thus, for example, more than 100 naphtha-based hydrogen plants with a total capacity approximately corresponding to the H_2 production from 5 million t/y of methanol are being operated in India, China and Japan [HAID KOSS 2001]. Replacing naphtha as a feedstock for hydrogen production by methanol thus represents a further promising challenge for the methanol industry.

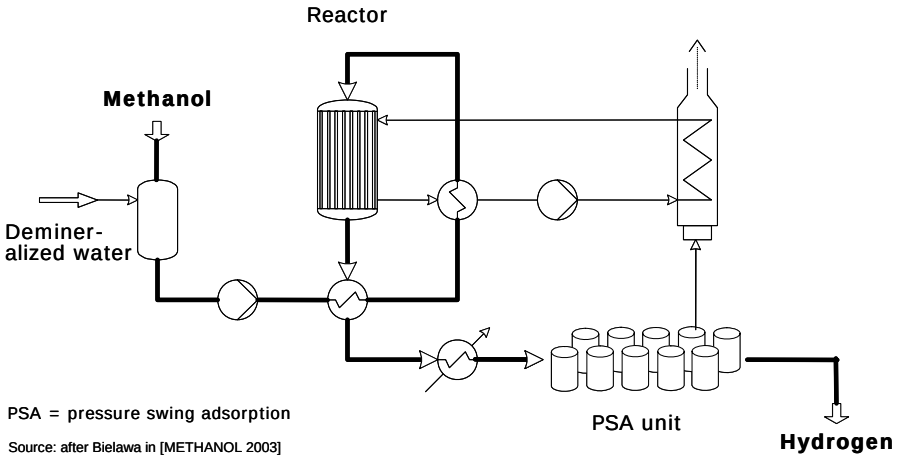


Figure 41: *MTH®* process [HAID KOSS 2001]

The methanol-to-hydrogen process *(MTH®)* (**Figure 41**) is a mature and proven technology, which has been applied in more than 50 smaller plants (capacity < 2,000 Nm^3_{H2}/h) worldwide. Hydrogen is produced here by a combination of methanol reforming with a cleaning step, pressure swing

adsorption. The process benefits from the very low reaction temperature of approx. 250–300 °C in comparison to steam reforming.

In the past, the availability of low-cost methanol has been a limitation to the application of the *MTH®* process. If low-cost methanol is available, however, this technology can be scaled up without any problems to achieve very high H_2 production capacities, since only standard equipment is needed [HAID KOSS 2001].

In the *MTH®* process, a mixture of methanol and demineralized water is first compressed to the reaction pressure of about 25–30 bars. This mixture is preheated in a heat exchanger, which is operated with hot synthesis gas from the reactor to increase the energy efficiency of the process. Final heating and vaporization takes place in a second heat exchanger fed with the same heating medium that also heats the main reactor.

The methanol/steam mixture is converted into hydrogen and carbon dioxide in a simple, low-cost and easy-to-handle tubular reactor at low temperatures of 250–300 °C on a Cu/Zn catalyst:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3\ H_2$$

The inverse water-gas shift reaction proceeds in parallel to this heterogeneously catalysed reforming reaction, so that the product gas also contains carbon monoxide:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

The heat required for the reforming reaction is introduced by a heating medium loop. The heating medium is in turn heated in a tube bundle in a fired furnace.

Table 25: Economic efficiency of the *MTH®* process [HAID KOSS 2001]

Characteristics and costs	**MTH®**	**Steam reforming** (naphtha-based)
Feedstock consumption / (t / h)	60.3	35.0
Feedstock costs / (US$ / t)	90 [1]	150
Total fixed costs (EPC) / (million US$)	33	46.5
H_2 product value (EPC) / (US$ / t)	710 [2]	745

[1] Methanol: 90 US$/t ≈ 4.5 US$/GJ (**Table 2**) ≈0.0045 €/MJ (**Figure 2**);
[2] Hydrogen: 710 US$/t ≈ 6 US$/GJ (**Table 2**) ≈0.006 €/MJ (**Figure 2**);
EPC = *engineering, procurement and construction*

After cooling the product, the remaining gas impurities are separated from the hydrogen product by means of a pressure swing adsorption unit. The off-gas from the PSA unit is used for firing the furnace.

In **Table 25**, the comparison of *MTH®* with conventional steam reforming is based on the following assumptions:

– plant with a production capacity for H_2 of 100,000 Nm^3/h,
– filling stations and infrastructure for methanol and naphtha are not included,
– depreciation: 10% per year,
– ROI before taxes: 20%.

The figures show that methanol as a feedstock for hydrogen production can compete with naphtha as a feedstock for the steam reforming process.

7.4 Synthetic fuels

Fuels are conventionally produced by refining from crude oil, but they can also be synthetically produced from various carbonaceous raw materials. The raw material to which the greatest attention is given today is natural gas. Due to the concentration on natural gas, the processes for the production of synthetic fuels are also designated GTL technologies (gas-to-liquids) (cf. also [GTL 2003]).

The first and best known technology for the production of synthetic fuels is the Fischer-Tropsch (FT) process, which was developed in Germany in the twenties of the past century [FISCHER TROPSCH 1926]. However, the commercial application of the FT process was greatly restricted, apart from the special circumstances for use in Germany during World War II and in South Africa due to the economic embargo.

There are numerous aspects that illustrate the significance and attractiveness of synthetic fuels (**Table 26**) [DIESELNET 2003]:

– synthetic fuels are compatible with conventional engines and can therefore be used without modifications to the engine concepts,
– synthetic fuels are compatible with conventional fuels (comparable energy density, miscibility with conventional fuels, transport using the existing infrastructure),
– the fuels can be designed according to the requirements concerning performance and emissions,

– synthetic fuels can be used in the pure form, but can also be added to conventional fuels as a blend to improve their properties,
– the sulphur content of synthetic fuels is practically zero, which makes synthetic fuels compatible with a number of sulphur-sensitive exhaust gas cleaning concepts.

Potential sites for economically efficient GTL plants are in regions, in which very low-cost natural gas is available, as in the Middle East or in West Africa. GTL technologies are of particular interest at locations where natural gas (as associated gas) must be stored again or even be flared due to the lack of markets. Hydrocarbons could be produced there with GTL plants and can then be refined or directly shipped to the markets as refined products in conventional tankers.

Table 26: Comparison of synthetic fuels ([KÖMPEL LIEBNER 2002], [LIEBNER 2006])

Products and characteristics	*MtSynfuels*® process	FT synthesis	European specification from 2005 (2009)
Product slate			
Naphtha :kerosene+diesel		1:2.3 to 1:6	
Gasoline: kerosene+diesel	1 : 8		
Product properties		1	
Gasoline fuel			
Aromatics / (vol%)	11	<1	max. 35
Benzene / (vol%)	<<1	<<1	max. 1
Sulphur / (ppm)	<<1	<1	max. 50 (10) 3
Olefins / (vol%)	6	>30	max. 18
RON	92	<40	91/95/98 2
MON	80	<40	82.5/85/88 2
Diesel fuel			
Polyaromatics / (vol%)	<<1	<1	max. 11
Sulphur / (ppm)	<<1	<5	max. 50 (10) 3
Cetane number	>52	>70	min. 51

1 properties of FT naphtha; 2 RON/MON for: Regular Gasoline/Euro-Super/Super-Plus; 3 diesel with 10 ppm sulphur has to be available on the market;

A future-oriented technology for the production of synthetic fuels is the *MtSynfuels*® process (**Figure 42**). It combines the *MegaMethanol*® tech-

nology with the *MTP®* (methanol-to-propylene) process and subsequent conversion of olefins into diesel *(COD)*.

The *MegaMethanol®* technology was already described in detail in **Chapter 7.1**. The *MTP®* process is an innovative technology, which closes the chain from the "waste material" natural gas (as associated gas) to valuable chemical products. Starting out from natural gas and passing through methanol and DME (cf. *MTD, MegaDME*, **Chapter 7.2.1**) a methanol/DME/water mixture is produced here, which is converted to propylene as the main product and to other olefins and alkanes as byproducts in several reactor stages. The product mixture can be separated into propylene (chemical grade, purity > 97%), LPG, gasoline and fuel gas using standard separation processes [HOLTMANN 2001]. In the *MTP®* process as an intermediate step for the production of synthetic fuels, this separation of the product mixture is clearly reduced.

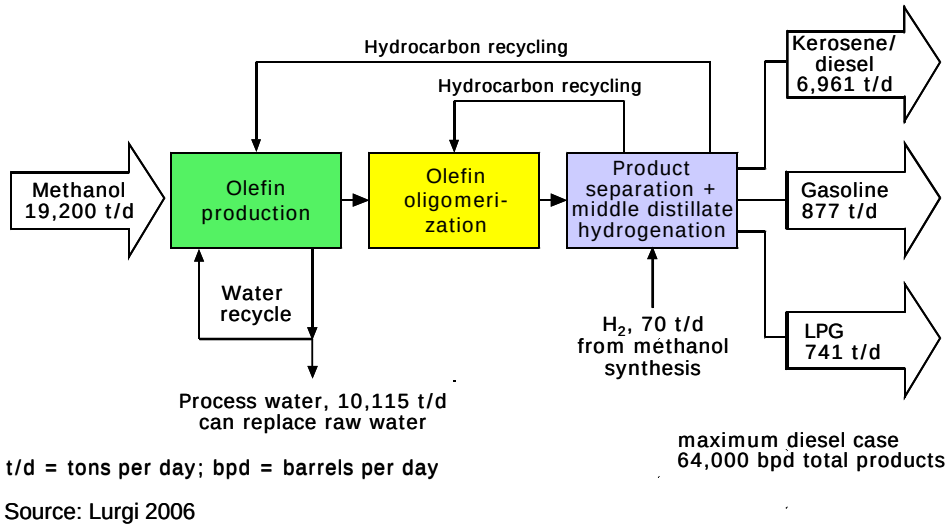


Figure 42: Gas-based refinery via methanol: Lurgi's MtSynfuels® [LIEBNER 2006]

After more than 9,000 operating hours of a pilot plant and with the demonstration plant gone into operation in Norway in January 2002, which has meanwhile confirmed the required catalyst life with over 8,000 operating hours, the *MTP®* technology has become marketable (two commercial orders as of early 2006, below). Since propylene is mainly an intermediate product, the propylene produced by *MTP®* has already been used in polymerization. The products produced in this way (drinking cups of polypropylene) have recently been presented to the public. They represent the

first consumer good produced from natural gas and clearly illustrate the bridging from natural gas to a valuable product.

The *MTP®* process is an exemplary technology for the pioneering route from natural gas to valuable petrochemical products (gas to petrochemicals). These technologies serve to develop ecologically and economically lucrative alternatives to the oil-based production routes. Nearly all process steps are technically proven. The economic efficiency of these alternative routes mainly depends on the ratio of the natural gas price to the crude oil price and is increasingly given with further crude oil shortage.

The *COD* technology was applied as early as 1992 in a plant in South Africa and has proven its reliability since the plant was put into operation in 1993.

The *MtSynfuels®* process is used to produce kerosene and diesel as the main products and gasoline and light oil as byproducts from methanol in the multistage process described. The individual process stages are interlaced through raw material recycling.

The comparative economic analyses of synthetic fuels summarized in **Table 27** and **Table 28** are based on the following assumptions:

– plant site: Middle East,
– plant capacity: 64,000 bbl/d of products,
– natural gas price: 0.70 US$/MMBtu,
– depreciation: 10% for installations inside the plant boundaries, 5% for installations outside the plant boundaries,
– ROI: 10%,
– the total plant capital comprises costs for installations inside and outside the plant boundaries as well as 20% for further project costs,
– the production costs comprise the depreciations and 10% ROI,
– market price of the product: as of 2005 including transport costs (shipping Middle East) according to tariffs for the regions considered
– budgetary estimate (as of 2005) with ±30% accuracy (cost increase 2005 —> 2006 may be in the 20% range!).

Table 27 shows that *MtSynfuels®* can compete well with existing FT plants. Even if the complete large-scale application of the *MtSynfuels®* process is still outstanding – this also applies to most of the currently discussed FT processes – this process has nevertheless already proved efficient in three of the four process steps. For the still outstanding step *(MTP®)* the operation of the demonstration plant since 2002 has confirmed

laboratory measurements on the one hand. Successful scale-up on the other hand has led to commercial orders for plants of 120 kt/a and 470 kt/a of propylene respectively (as of early 2006).

Table 27: Comparison of capital and cost estimates for synthetic fuels [LIEBNER 2006]

Capital and specific costs for	*MtSynfuels*® process	Modern FT synthesis
Total capital investment / (million €)	1,797	1,809
Specific total plant capital / (€/bbl per day)	23,490	23,650
Natural gas [1] to process (LHV) / (€/bbl)	5.18	6.25
Natural gas to utilities (LHV) / (€/bbl)	1.06	0.3
Catalysts & chemicals / (€/bbl)	2.63	2.3
Cost of production + ROI 16%/ (€/bbl)	28.2	28.1
Cost of production + ROI 25%/ (€/bbl)	35.9	35.8

[1] natural gas @ 0.54 €/MMBtu

Table 28: Comparison of market prices for synthetic fuels ([KÖMPEL LIEBNER 2002], [LIEBNER 2006])

Fuel	Western Europe	USA	Japan
gasoline / (US$/bbl) [1]	34.75	31.42 [2]	29.70
diesel / (US$/bbl) [1]	28.88	26.51 [2]	33.21
gasoline / (€/bbl) [3]	43.8	39.6 [4]	n.d. [5]
diesel / (€/bbl) [3]	37.2	41.2 [4]	n.d. [5]

[1] as of 2001; [2] Gulf Coast; [3] corresponding crude oil price: ~ 42 $/bbl (for comparison: ~ 70 $/bbl in quarter 2 of 2006); [4] US Nymex; [5] no data available

7.5 Summary of Chapter 7

There are large natural gas deposits that are suitable for use as low-cost raw material for methanol production. This would lead to a better utilization of natural resources, especially in the case of associated gas, which – unless profitably used otherwise as in the case of *MegaMethanol*® – would be flared off. The conversion of methanol into DME and propylene considerably increases the value of natural gas as a feedstock and involves an

enormous potential for growth and high ROI, the definitely most successful motivation for environmental protection.

The *MegaMethanol*® technology cuts the production costs for methanol to such an extent that a completely new range of downstream products such as DME, propylene and synthetic fuels is opened up. Based on simple fixed-bed reactor systems, conventional process components and operating conditions – including commercially produced catalysts – the *MegaDME*, *MTP*® and *MtSynfuels*® technologies open up ecologically and commercially attractive routes to the use of natural gas, especially associated gas.

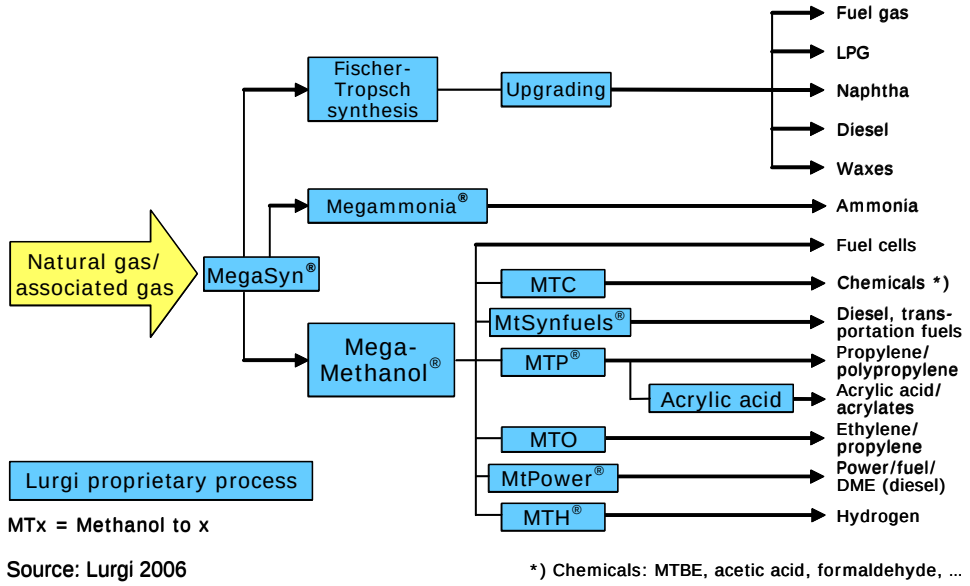


Figure 43: Lurgi's gas-to-chemicals processing routes (GTC®) [LIEBNER 2006]

Based on the combination of highly efficient concepts and low investment costs, special technology chains have been developed starting out from natural gas and passing through methanol to DME, propylene or polypropylene and synthetic fuels. In the next step, these concepts then lead to gas-based refineries and gas-based petrochemicals.

Figure 43 summarizes this route from natural gas to fuels and valuable chemical products (gas-to-chemicals, *GTC*®), illustrating the central role of methanol (bottom branch of the diagram). The possibilities of using methanol as a fuel and thus as an energy carrier for transport and traffic are diversified (methanol fuel cell, methanol combustion engines, synthetic fuels (diesel, gasoline, kerosene etc.), hydrogen, electricity). The

additional new development of the use of methanol as a feedstock for the petrochemical industry could also produce synergy effects. Due to a further reduction in production costs and independence of the oil price and the associated fluctuations, methanol production on a large technical scale worldwide would make the use of methanol as a fuel even more attractive because of permanently low methanol prices.

8 Hazard potentials of methanol

With a view to the infrastructure, transport, storage, handling and use of natural gas, hydrogen or methanol for energy conversion systems, questions arise concerning safety-related modifications in comparison to the use of conventional fuels and energy conversion systems.

Table 29: Properties of methanol, methane and hydrogen in comparison to gasoline (after [MPE 2000], [METHANEX 2003], [HANISCH 2001], [PIRNIE 1999])

Fuel	Gasoline	Methanol	Methane (NG [1])	Hydrogen
Density ratio ρ_{fuel}/ρ_{air} /(-)	3.2–4	1.1	0.55	0.07
LHV [2]/(MJ/kg) LHV [2]/(MJ/dm^3)	43.9 32.5	19.9 15.8	40–47 36.9	120 10.8E-3
Reid vapour pressure (@37.8°C)/kPa	45–90	32	–	–
Ignition temperature/°C	220	455	595	560
Ignition range/(vol% in air)	0.6–8	5.5–44	5–15	4–76
Minimal ignition energy/mJ	0.24	0.14	0.28	0.02
Diffusion coefficient in air/(cm^2/s)	0.05	0.12	0.16	0.61
Laminar combustion velocity/(m/s)	0.4	0.48	0.43	2.7
Flash point/°C	-20	11		
Vaporization heat/(kJ/kg)	350	1,110		
Solubility in water/%	0	100		
Lethal oral dose/ml	500	30–100		
Odour threshold/(ml/m^3)	0.06–0.08	1,500–1,900		
Half-live for biological degradation in soil a/o water/d	benzene: 5–16	1–7		
TLV [3]/ppm	toluene: 50 xylene: 50	200		

[1] NG = natural gas; [2] LHV cf. also **Table 38**; [3] TLV = threshold limit value

Answers are obtained by considering the safety-related properties of the energy carriers (**Table 29**), protective measures concerning production,

transport, storage and system integration (e.g. in vehicles or CHP packages) and operating instructions for the customer.

The hazard potential of methanol essentially concerns the areas of safety, environment, health and filling stations, for which statements after [HANISCH 1985], [HANISCH 2001], [WHO 1997] and [MFCA 2003] are summarized in the following.

8.1 Safety

Methanol is a physically and chemically well-defined substance, which has been produced for decades on a large technical scale and does not present any serious problem as far as the technology is concerned.

The odour threshold for methanol is high; a reduction by adding odorous and flavouring substances is conceivable (a Californian regulation already requires such additives). However, the compatibility of these additives must be ensured for heterogeneously catalysed methanol reforming [XCELLSIS 2002].

Methanol vapour is slightly heavier than air; explosive mixture can form with air. Due to the lower vapour pressure in comparison to gasoline, ignitable mixtures may form in the tank, so that closed refuelling systems and an adapted safety technology should be provided. The customer must not get into contact with methanol during fill-up. According to the present state of the art, refuelling could be performed in closed systems [MFCA 2003], [IDENTIC 2000].

The fire hazard is lower for methanol than for gasoline [MFCA 2003]. This is due to the lower volatility, higher ignition temperature, lower heating value and higher vaporization enthalpy of methanol. Fire-extinguishing powders and CO_2 are used for small fires and AFFF foam for major fires.

Methanol is a colourless, volatile and highly flammable liquid with a typical smell. The flame visibility is comparable to that of hydrogen, slightly bluish, not visible in bright sunlight. In case of a fire, however, the flame is visible because other substances also burn [METHANEX 2003]. Californian regulations for handling methanol (M100) do not prescribe any additives to the methanol for making the flame visible, but an on-board flame arrester to prevent flashback [XCELLSIS 2002].

The use of methanol in road traffic would double the deployment of tankers on the roads due to the about 50% lower volume-related heating value compared to gasoline/diesel (**Table 25**) and thus increase the num-

ber of tanker accidents assuming the same frequency. Compared to gasoline, however, the fire hazard would be lower.

8.2 Environmental impacts due to leakages

Methanol is degradable in the environment due to processes of photooxidation and biodegradation; in soil some microorganisms can take up methanol for growth and degrade it to water and carbon dioxide.

In the case of small leakages, methanol has only a minor toxic effect on waters and soils. In soil methanol is more readily degradable than gasoline. High concentrations of methanol make biodegradation in waters and soils increasingly difficult. Concerning the volatility of methanol from water cf. Henry coefficient (**Chapter 14.2.2** and **Table 36**).

The lethal methanol dose, LD50, for 50% of a population of rats, mice and dogs examined is in the range of 6,200–13,000 $mg_{methanol}/kg_{body}$ weight [WHO 1997]. For freshwater fish the LD50 value of methanol is 13,000–29,000 $mg_{methanol}/l_{water}$ for an exposure of 96 h. It is thus clearly higher than for a corresponding exposure to gasoline [WHO 1997], [MFCA 2003].

8.3 Human health

Humans are endangered by the oral or inhalative uptake of methanol especially during refuelling. Additives to methanol, which increase the taste and odour thresholds, as well as closed refuelling systems can minimize this danger.

Of medical relevance is above all the miscibility of methanol with water and organic compounds, which is possible in any ratio, as well as the solvent power in fat, although this is low. Methanol can be contained in dietetic food and soft drinks via the artificial sweetener ASPARTAM [WHO 1997].

The toxicokinetics of methanol is known. Oxidative processes produce formaldehyde and formic acid as the actually toxic metabolite. Methanol has a slightly irritant effect if taken up via the skin, eyes and respiratory system. Depending on the dose, the oral and inhalative uptake of methanol can lead to blindness (above 5–15 ml) or death (above 30–100 ml). A complete healing of possible poisoning effects is possible if established methods of treatment are applied rigorously and in time. There are no clues for any carcinogenic, mutagenic or teratogenic effect.

8.4 Filling stations

In connection with a BMFT research project from the eighties on alcohol fuels, the German Committee on burnable fluids (DabF) made a safety-related statement in 1980 [HANISCH 2001], according to which DabF has no safety-related objections to the construction of filling stations for methanol fuel, provided that the applicable regulations are complied with. According to the present state of the art, refuelling could be performed in closed systems [IDENTIC 2000] and [MFCA 2003].

The requirements to be fulfilled by materials used in fuel systems (metals and elastomers) with respect to their resistance to methanol are well known and imply a corresponding expenditure on building up a suitable supply network [HANISCH 2001].

If used in accordance with regulations and if all relevant rules are observed, handling methanol does not represent any health or safety problem [HOMMEL 1997], [EU 1991].

8.5 Comparison with possible direct fuel cell fuels

The acute toxicity of methanol is often cited as a disadvantage. However, it is much less toxic than gasoline as the established energy carrier which we are used to handle today. In contrast to methanol, gasoline is also carcinogenic and teratogenic. Methanol is much more easily biodegradable than gasoline or diesel. Due to its solubility in water, methanol can penetrate through the skin into the human body during handling, but this can be prevented by protective measures. **Table 30** shows a comparison of the properties and suitability of alternative energy carriers, especially methanol, with hydrogen and gasoline, all of which are in principle possible energy carriers for use in direct fuel cells. Methanol comes off best in this comparison [HEINZEL et al. 2006].

Table 30: Methanol in comparison with possible direct fuel cell fuels (after [HEINZEL et al. 2006])

Energy carrier {CAS-Nr.}	Methanol [1] {67-56-1}	Dimethyl ether [2] {115-10-6}	Ethanol [3] {64-17-5}	Hydrogen [4] {01333-74-0}	Gasoline fuel [5] [a]	
					> 90% Gasoline (unleaded) {86290-81–5}	< 1% Benzene {71–43-2}
General						
State @ 20°C	liquid	cryogenically liquefied gas	liquid	gaseous	liquid	liquid
Possible hazards	decomposition products in case of fire: CO, CO_2, CH_2O; explosive mixtures with air possible	cold burn/ frostbite, suffocation	vapours are heavier than air; explosive mixtures with air possible	at high concentrations: narcotization, suffocation	dangerous decomposition products possible in case of incomplete combustion	
Density/(kg/m³) @ 15°C [6]	*793*	*670*	*794*	*0.09@1.013bar*	*750* [6]*,725–780* [5]	*880 @ 20°C* [7]
Solubility in water/(mg/litre) @ (20°C, 1 bar)	complete	n.r.d.a.	miscible	1.6	non-miscible	1,000.8 [7]
Performance data						
Energy density/(MJ/l) [6]	*16*	*19*	*21*	*3 @ 300 bar*	*32*	*n.k.*
Technically attainable current density/(mA/cm²), power density/(mW/cm²)	250 @ 400mV, 100 @ 70°C [9]	20 @ 400mV, 8 @ 70°C [10]	25 @ 400mV, 10 @ 70°C [11]	1,000 @ 700mV, 700 @ 70°C [12]	n.a.	
Toxicity						
TLV/ppmv	200	1,000	500	n.a.	n.a. [b]	n.a.
TRC/ppmv	./.	./.	./.	n.a.	300 [c]	1
LD50 rat oral/(mg/kg)	5,628	tox. n.k.	7,060	no tox.	n.i.	930 [7]
LC50 rat inhalative/ppm	64,000 @ 4h	tox. n.k.	38.3 mg/l @ 10h	no tox.	3,400 @ 4h	44 mg/l @ 4h [7]
LC50 fish toxicity/(mg/l)	10,800 @ 96h	tox. n.k.	8,140 @ 48h	no tox.	toxic (**R51/53**)	5 @ 96h [7]
Teratogenic substance [d]	no [8]	tox. n.k.	no	no tox.	n.k.	yes [7]

WHC / water hazard	1 / weak	1 / weak	1 / weak	0 / none	3 / great	3 / great [7]
log P(o/w)	-0.82 / -0.66	n.k.	-0.32	n.k.	> 3	2.1 [7]
Biodegradability	easy (water)	n.k	easy	n.k.	potentially yes	easy [7]
Carcinogenic (**R45**)	no	no	no	no	yes (**R45**)	yes (**R45**)
Danger of fire / explosion						
Flammability	ready	high	ready	high	high	ready
Explosion limits in air/vol%	6–36	3–18.6	3.4–15	4–77	0.6–0.8 (low)	1.2–8 [7]
Applicability for direct fuel cells						
OVERALL EVALUATION	**GOOD**	**FAIRLY GOOD**	**DEMANDING**	No evaluation, comparison only !		
power density (DFC)	high	moderate	low	n.a.	n.a.	n.a.
storage density (EC)	high	high	high	low	very high	n.a.
handleability (EC)	good if safety measures are observed	good	simple	fairly good	good if safety measures are observed	in laboratory only, highly toxic !

Abbreviations: DFC = direct fuel cell; EC = energy carrier; TLV = threshold limit value; TRC = technical reference concentration; WHC = water hazard class; log P(o/w) = n-octanol/water distribution coefficient; n.a. = not applicable; n.i. = no information available; n.k. = not known; no tox. = no specific toxic effect; n.r.d.a. = no reliable data available; tox. n.k. = toxic effects not known.

Remarks: [a] naphtha, not specified; possible: oxygen compounds, additives; [b] BP: Material Safety Data Sheet Avgas 100LI (>0.1% benzene), 14.06.2002; [c] recommendation: workplace limit value ACGIH / USA; [d] according to DFG recommendation.

Risk phrases (according to EC Directive 67/548/EEC): **R45** = may cause cancer; **R51/53** = toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Sources: [1] Methanex: Material Safety Data Sheet, methanol; 25.11.1996; [2] Air Liquide: EC Material Safety Data Sheet acc. to Technical Regulations for Dangerous Materials (TRGS) 220; 01.07.2004; [3] Hedinger: EC Material Safety Data Sheet, absolute ethanol, 11.11.2003; [4] Air Liquide: EC Material Safety Data Sheet acc. to TRGS 220; 15.02.2002; [5] BP: Material Safety Data Sheet, regular gasoline 91 / premium 95 / premium plus 98 unleaded; [6] CONCAWE, December 2003 Well-to-wheels analysis of future automotive fuels and power trains in the European context (source applies to whole line in the table above); [7] Hedinger: EC Material Safety Data Sheet, benzene; 21.06.2004; [8] Hedinger: EC Material Safety Data Sheet, methanol; 27.03.2003; [9] A.S. Arico, J. of Power Sources 127 (2004) 112–126; [10] 5th FCDIC Fuel Cell Symposium, Proceedings, 14–15 May 1998; [11] C. Lamy, Elect. Chemica Acta 49 (2004) 3901–3908; [12] O. Teller, W.L. Gore, Paper 2nd PEFC Forum Lucerne 2003.

8.6 Summary of Chapter 8

If used in accordance with regulations and if all relevant rules are observed, handling methanol does not represent any health or safety problem. The use of methanol in road traffic would double the deployment of tankers on the roads due to the about 50% lower volume-related heating value compared to gasoline/diesel and thus increase the number of tanker accidents assuming the same frequency. Compared to gasoline, however, the fire hazard would be lower. Humans are endangered by the oral or inhalative uptake of methanol especially during refuelling. Additives to methanol, which increase the taste and odour thresholds, as well as closed refuelling systems can minimize this danger.

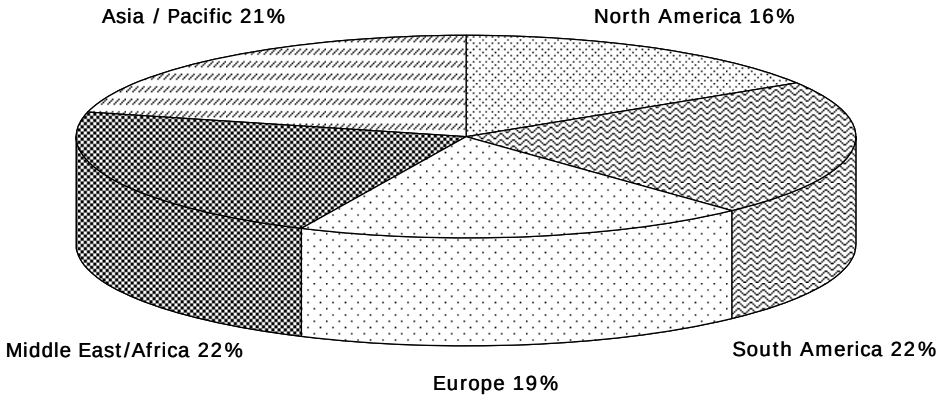
The acute toxicity of methanol is often cited as a disadvantage. However, it is much less toxic than gasoline as the established energy carrier which we are used to handle today.

9 Methanol for the chemicals market [14]

More than 80% of the methanol produced worldwide is obtained from natural gas today. In Germany, residues from refineries are used as energy raw materials. An essential advantage is that methanol can be produced in the same quality from fossil raw materials and from renewable primary energy carriers. Along with a significantly further rising demand for natural gas, a stable and in future rising methanol price is expected, so that the attractiveness of a methanol production from other even more expensive input products than natural gas will rise in the long term.

9.1 Global production capacities

In 2002, methanol production capacities of 37 million t were installed worldwide [McCASKILL 2002]. Methanex as the largest company had the highest market share (17%) with approx. 6 million t installed capacity worldwide in 2000, followed by the Saudi Methanol Company and Celanese [FISLER 2000]. According to a study by Chemical Market Associates [CMAI 2001], global methanol capacities will not significantly increase up to 2004.



Source: after Erdmann/Schlecht in [METHANOL 2003]

Figure 44: Global market shares of methanol capacities according to regions in December 2001 [METHANOL 2002]

[14] Chapter 9 is based on: Erdmann/Schlecht in [METHANOL 2003], Chapter 7.

The market shares of the production capacities according to regions in December 2001 are shown in **Figure 44**. South America and the Middle East including Africa have the greatest share of 22%. Both regions export methanol especially to Europe and North America.

The biggest market players among the methanol producers in Europe are compiled in **Table 31**. The ICI and Methanor plants use natural gas as the input product for methanol production, whereas the other plants use liquid and gaseous residues from the oil industry. In the 1990s, total capacity and output increased by 38%. The European producers increased their global market share by 2% to 23% [VRIENS 2000].

Table 31: European methanol production: capacities and changes 1990–1999 [VRIENS 2000]

Production in Europe	**Capacities / 10^3 t**		**Changes / %**
Years	1990	1999	1990–1999
Producers			
BASF (D)	240	450	+88
Chem Linz (A)	110	n.d.	n.d.
DEA (D)	400	380	-5
ICI (GB)	500	450	-10
Leuna (D)	660	660	0
Methanor (NL)	750	850	+13
Statoil (N)	n.d.	850	n.d.
SVZ (D)	n.d.	120	n.d.
VEBA (D)	240	240	0
Total capacity	2,900	4.000	+38
Estimated output	2,400	3.300	+38

n.d. = no data available

9.2 Global demand for methanol

In the year 2002, 36% of the global demand for methanol was used for the production of formaldehyde [METHANOL 2002]. Formaldehyde mainly serves to produce polycondensates such as melamine, phenolene or urea.

The second third of methanol demand amounting to 7.5 million t in 2002 served for the production of methyl tertiary-butyl ether (MTBE) [METHA-

NOL 2002]. Instead of the formerly used organic lead compounds, MTBE is admixed to gasoline fuels as an anti-knocking agent. 57% of the global MTBE demand was needed by the USA in the year 2000. In the same year, the United States imported 30% of the global MTBE production. California alone claimed 20% of the global MTBE demand in 2000. 43% of the installed MTBE production capacities worldwide were located in the USA in 2000, the remainder was covered by imports especially from the Middle East, Canada and Venezuela. Until recently MTBE essentially contributed to the growth of the methanol market [FISLER 2000].

With the introduction of the 1990 Clean Air Act Amendments the year-round use of reformulated gasoline (RFG) is required in cities with great summer smog problems. On balance, reformulated gasoline produces fewer emissions of ozone-forming and toxic air pollutants with the same fuel throughput as conventional gasoline. This fuel contains a fraction of at least 2wt% (or 11vol%) of chemically bound oxygen (oxygenate), which is obtained with the aid of MTBE [DOE 2003] (for comparison, most of the fuels used in Germany contain clearly less MTBE than the Californian fuels).

Due to the lack of storage regulations for fuels, pipeline and tank leakages are nothing unusual in the USA. Major MTBE contaminations in groundwater already occurred there in the mid-nineties. Only after the introduction of reformulated gasoline with an MTBE fraction of 11vol% was it recognized that MTBE is poorly degradable and very mobile in soil. The addition of MTBE to reformulated gasoline has been prohibited in California since the end of 2003 (cf. **Chapter 11.2**).

7% of the methanol produced worldwide was used for the production of acetic acid in 2002. This mainly served as the base product for various acetic acid esters: as a monomer for vinyl acetate and as cellulose acetate in artificial silk production. Furthermore, acetic acid finds application as a solvent for lacquers and resins, in inorganic salts as an additive in the clothing industry, in dye works and in medicine.

3% of the methanol produced worldwide was further processed to methyl methacrylate (MMA) in the same year. MMA is used in chemical production as a monomer for the fabrication of acryl glass. Another methanol fraction of approx. 2% was used for the production of dimethyl terephthalate (DMT). DMT is used, in particular, for the production of polycondensates, above all polyethylene terephthalate (PET).

Approx. 20% of the methanol produced worldwide in 2002 covered the demand in various fields of application [METHANOL 2002].

In 1999 in Western Europe 49.5% of the methanol was used for formaldehyde production. Another 16.5% was used in MTBE production [VRIENS 2000]. According to the Commission of the European Union (EU) there is no need for action concerning the replacement of MTBE in gasoline fuel. Unlike the American legal requirements for fuel, the EU fuel directive does not stipulate minimum values for MTBE, but a maximum oxygen content [EU 1998]. The Danish government pushes the replacement of this fuel additive by imposing a tax of 0.67 €/l on MTBE [T&E 2000].

9.3 Prospects for global methanol demand

The determining factor for methanol demand is the sales development in the chemical industry. The economic development in the chemical sector follows the gross national product (GNP) [HOPP 2001]. The GNP is a national economy indicator for the development of markets and it characterizes the value of all goods and services having a market price and being consumed, invested or exported by citizens during a defined period. The GNP is reduced by the value of all imported goods and services. GNP growth can thus be transferred to methanol sales and thus to the demand for methanol.

However, the production of acetic acid grows more strongly than the GNP. The demand for methanol rises correspondingly faster in this segment. This may be due to the fact that a technology shift from ethylene (oxidation of ethylene or of acetaldehyde from ethylene [WACKER 2003]) to methanol (methanol carbonylation [CELANESE 2003]) as the base product for acetic acid production has taken place in recent decades [McCASKILL 2000].

If the ban on MTBE[15] is enforced in California, 20% of the MTBE demand will break away worldwide. This will affect, in particular, sites with high production costs in the USA. Should these production capacities not be shut down, their production will press as MTBE exports on the world market, which would probably result in a global price decline for MTBE. Irrespective of this, a cost-induced decrease of production capacities is already to be expected in North America in the medium term. Chemical Market Associates (CMAI) expect that two thirds of the methanol capacities in the USA will be cut down by 2005 [FISLER 2000]. However, new production facilities are being built in South America, Africa and the Middle

[15] cf. **Chapter 11.2**

East, so that the pressure on the methanol price is likely to be maintained.

9.4 Methanol trading

Methanol imports to Western Europe increased by 27% from 1991 to 2000 [VRIENS 2000]. The importation of methanol from Trinidad and Venezuela did not diminish domestic methanol production, but took place at the expense of Saudi Arabia and Russia as the main importers. Trinidad has been the largest exporter of methanol since 2000 and has replaced Saudi Arabia [METHANOL 2002]. It is obvious that the rising demand for methanol in the Middle East provided better sales markets for Saudi Arabia than the transport over long distances to Western Europe. The imports to the EU and EFTA are shown in **Table 32** for the years 1991 and 2000.

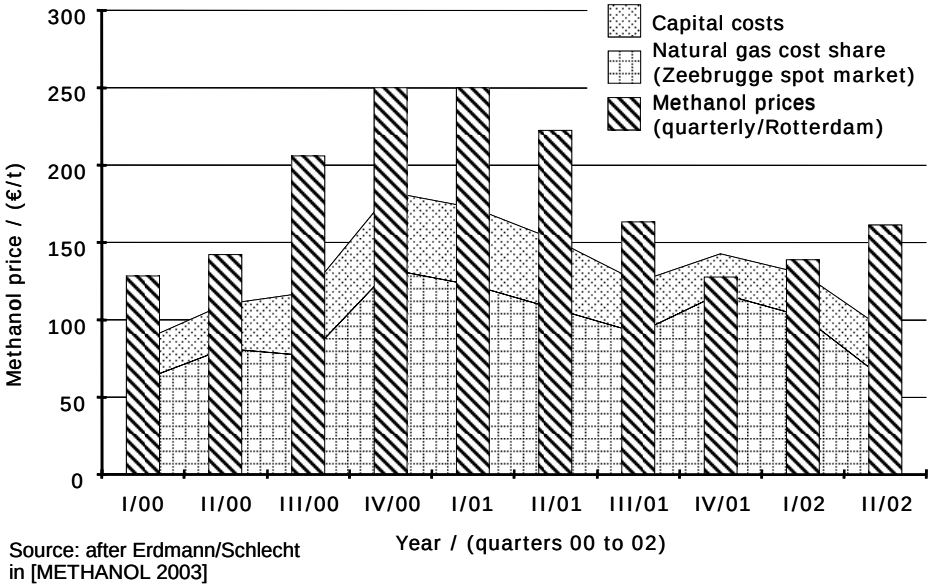
Table 32: Methanol imports to EU and EFTA states in the years 1991 and 2000, quantities/kt [VRIENS 2000]

Countries and quantities	1991	2000
Exporting countries		
Saudi Arabia	800	400
Russia	700	200
Libya	625	525
Chile	325	770
Algeria	75	95
Trinidad	50	900
Central Europe *	100	100
Venezuela	0	450
Others	75	60
Total quantities	2,750	3,500

* Bosnia, Bulgaria, Croatia, Czech Republic, Herzegovina, Hungary, Poland, Macedonia, Rumania, Serbia with Montenegro, Slovakia, Slovenia

Similarly to natural gas imports, European methanol imports are mainly handled on the basis of long-term supply contracts with price escalation clauses. The prices are always adjusted at the beginning of a new quarter. A comparison of the methanol price with pro-rata natural gas costs

(**Figure 45**) shows that both price developments exhibit about the same rising trend for the year 2000. The natural gas costs are based on the Zeebrugge spot quotation (market price). In 2001 both the methanol prices and the prices of natural gas as costs factors for methanol production largely show a falling trend. The capital costs are, relative to the methanol price, a constant cost component in 2000 and 2001.



Source: after Erdmann/Schlecht in [METHANOL 2003]

Methanol in II/02: 150 €/t ≈ 8 €/GJ (**Table 2**) ≈0.008 €/MJ (**Figure 2**)

Figure 45: Cost structure of methanol in comparison to the price of methanol in Europe (quarters of the years 2000 to 2002)

The official contract prices for methanol relate to Rotterdam as the place of delivery, where the greatest unloading capacities in Europe are located. However, the prices paid are probably clearly below published Amsterdam-Rotterdam-Antwerp (ARA) quotations. Hidden price reductions are being assumed. For example, at the other European ports no higher prices than in Rotterdam are requested; consequently, the freight costs from Rotterdam to the other ports must be borne by the bidders. Methanex as the market leader is also leading the trend towards optimizing the logistics costs.

9.5 Methanol prices

There are numerous processes for the production of methanol. Each of these processes can be profitable under the respective production conditions such as capacity, availability, process type and costs of primary products, consumables and synergy potential.

The optimum conditions for low methanol production costs are:

– low costs of the feedstock to be used, often natural gas,

– high synthesis gas production capacities and yields,

– high synergy potential for the production of byproducts.

Methanol production plants exhibit significant economics of scale. These are understood to be decreasing unit costs with increasing production. Reasons for economics of scale are:

– more efficient production due to larger plants,

– use of improved production processes,

– degression of fixed costs per output unit with rising output,

– better purchasing conditions,

– learning effects.

Thus, the production costs, for example, for tandem reforming (two-stage reforming with oxygen import in the second stage) amount to more than 115 US$/t for production capacities of <1,000 t/d and decrease to 80 US$/t for production capacities of 3,000 t/d (in comparison, for steam reforming: >140 US$/t and approx. 100 US$/t for production capacities of <1,000 t/d and 3,000 t/d, respectively; approx. 105 US$/t for 2,500 t/d) [MICHEL 1999].

The published prices for methanol FOB Rotterdam were 145 US$/t in April 2002. In comparison, the spot price on the American Gulf Coast was only 125 US$/t in March. In the Asian/Pacific region the price per ton was between 132 and 147 US$. As for other energy carriers, the methanol prices were very unstable in the past two years. The price development in the year 2000 was determined by a loss of production capacities totalling 1.5 million t in the USA and Trinidad. Added to this were the high natural gas prices, which led to a methanol price of over 200 US$/t (1 US$/t≈1 €/t in **Figure 45**) in the last quarter of 2000 and thus to almost a doubling in comparison to the first quarter of 2000 [McCASKILL 2000]. In the course of the year 2001 the price dropped again to the level observed before. The causes include global economic slowdown and the already mentioned changes on the American market. A renewed price increase was recorded

in the first quarter of 2002. At the end of the same year, a price level of 200 US$/t was reached, which is likely to be maintained until mid-2003 [McCASKILL 2002].

Between 1985 and 1999 the methanol prices ranged between 100 and 200 US$/t with an average of 150 US$/t [MICHEL 1999]. The last cyclical price decline began in 1998 and was caused by an oversupply of methanol.

9.6 Future development

Methanol use in Europe is strongly focused on the chemicals market today [McCASKILL 2000]. Apart from the application as a fuel additive in the form of MTBE, methanol could also be directly used as a fuel for internal combustion engines or for fuel cell power trains. Another field of application could be the production of dimethyl ether as a substitute for diesel fuel, which would have the advantage of a particulate-free combustion in diesel combustion engines (cf. **Chapter 3** and **Chapter 7.2**).

The plastics-processing industry could also be a conceivable market for enhanced methanol use. Propylene, an important petrochemical base material for plastics production, has so far almost exclusively been produced from oil.

With its methanol-to-propylene process LURGI has developed a new process up to market maturity, with which propylene is produced from methanol, which in turn is obtained from natural gas. In view of an expected increase in propylene demand LURGI sees excellent market opportunities [LURGI 2002].

The ban on MTBE[16] discussed in the USA and initiated in California leads to an enormous pricing pressure on methanol as the primary product; LURGI therefore developed the MegaMethanol technology for production plants with capacities >1.5 million t/y. This reduces the specific investment costs. In view of the cost problems for the US methanol capacities, a continuing capacity reduction is to be expected in the USA, which could eliminate the current problem of overcapacities.

From the European perspective, the future methanol price will be significantly influenced by the natural gas price, as in the past. In the event of a further deregulation of the European natural gas markets, the pressure on

[16] cf. **Chapter 11.2**

the natural gas prices could continue to exist, especially in the market for bulk buyers of relevance here. But the impacts on the price level will remain modest according to many analysts. In fact, the bulk buyer natural gas prices greatly depend on the import gas prices, and even if the previous close price coupling to heating oil or heavy oil were replaced by other price formulae, a permanent decline in natural gas prices is not to be expected due to the anticipated massive investments in European gas supply alone. Consequently, the methanol price in Europe will rise rather than drop below today's price level in the medium term. This will be the case, in particular, if an effective climate protection policy is adopted at least in Europe, since this will directly result in rising natural gas prices, because the European power plants will increasingly use natural gas as the fuel with lower CO_2 emissions compared to coal for electricity production.

9.7 Summary of Chapter 9

The global development of the demand for methanol is assessed similarly among the experts. [McCASKILL 2002] assumes a continuous growth to 33 million t up to 2006, before there will be a decline in methanol demand to 31 million t in 2007 due to the American MTBE ban. In early 2008 he expects a renewed increase in methanol demand. [AL SAYED 2000] also assumes a global growth in demand of 2.2% for 1998 to 2004. A market study [RASCHKA 2003] shows that sales decline due to the ban on MTBE[17] in the USA is overcompensated in the longer term by the increasing demand for methanol of the chemical industry in the Asian-Pacific region. Methanol could achieve a genuine breakthrough, if it were – also in competition with other alternative fuels – increasingly used as a fuel. However, this is not perceivable at the moment. Therefore, the chemicals market will remain the most important growth and sales market for methanol for the time being.

[17] cf. **Chapter 11.2**

10 Biofuel projects [18]

In order to push the market launch of alternative fuels (natural gas, biofuels and hydrogen), the EU plans to introduce 8% biogenic fuels (corresponding to about 30 million toe) into the fuel market, 10% natural gas and 5% hydrogen up to the year 2020 [EU 2000], [EU 2001]. The driving forces are the Kyoto targets for CO_2 reduction and the decreasing dependence of the transport sector on crude oil imports. – See also [HEINLOTH 2002].

10.1 Overview

Theoretically, 8–14% of the agriculturally usable area in the EU is sufficient to reach the biofuel quota target. Another 8% would be needed if hydrogen were to be produced from biomass. At present, the set-aside area in the EU is about 6%. Additional important agricultural areas will become available due to the EU enlargement to the East. Waste materials and renewable electricity production represent an additional potential for biofuel and hydrogen production.

The resources of renewable energies for fuel production are sufficient to fulfil the political targets. The Transport Energy Strategy (TES) estimates the potential of biofuels (energy crops, waste and residual materials) at 15% of the total fuel demand of the 15 EU member states (EU15) (range 11–24%).

The basic processes for the production of renewable fuels have been investigated and are known in principle. At present, research projects are being implemented to obtain reliable data on energy balances, emissions and costs and to evaluate optimum concepts for economical fuel production (decentralized biomass procurement, decentralized and centralized fuel production).

Methanol can be relatively easily produced from biomass and can be used both in internal combustion engines (in the form of a fuel blend without engine adaptation or as pure fuel with engine modification) and in fuel cell systems (with on-board methanol reforming for PEFCs or directly for DMFCs).

[18] Chapter 10 is based on: Isenberg/Edinger in [METHANOL 2003], Chapter 8.

The EU targets concerning renewable fuels can be reached by the use of waste and residual materials for energy generation, of renewable electricity and of energy crops. The addition of renewable fuels to conventional gasoline or diesel does not require a new infrastructure during market introduction. Investments can be exclusively used for fuel production.

Demonstration projects will have to prove the environmental compatibility of renewable fuels, their availability, economic efficiency and suitability for use in vehicles in comparison to conventional fuels.

10.2 Production paths for biofuels

The use of fuels produced from renewable energy sources will be of increasing significance in the mobility sector. It may reduce traffic-related emissions, above all CO_2. Future fuel supply can be assured by broadening the supply base, especially by domestic energy carriers [ISENBERG 2001].

Biomass is a promising resource for environmentally compatible fuel production. Various processes can be used to convert biomass into fuels:

– oil extraction from oil-containing plants,
– fermentation of waste materials and energy crops (e.g. biomass with high sugar or starch content) to biogas or alcohols, especially ethanol,
– gasification of biomass and subsequent fuel production by synthesis to alcohols (e.g. methanol), Fischer-Tropsch fuels (synthetic diesel and gasoline) or hydrogen separation from synthesis gases.

For example, biomethanol can be obtained by the gasification of biomass to synthesis gas and subsequent methanol synthesis. As in the production of methanol from natural gas, after the production of a synthesis gas (CO, CO_2, H_2) methanol is obtained here by a heterogeneously catalysed synthesis dissipating heat (cf. **equation 4.2**).

$$\begin{aligned} CO + 2H_2 &\Leftrightarrow CH_3OH & -\Delta H &= 91\ kJ/mol \\ CO_2 + 3H_2 &\Leftrightarrow CH_3OH + H_2O & -\Delta H &= 49\ kJ/mol \end{aligned} \qquad \text{(eq. 4.2)}$$

CHOREN at Freiberg in Saxony are currently constructing a commercial biomass to liquid production facility. Once in operation the plant will convert 65,000 tons of biomass per year (dry substance) into liquid FT fuels [SCHULZE RUDLOFF 2006].

A second possibility of producing biofuels is the production of the fermentation alcohol ethanol (C_2H_5OH) by fermenting sugar ($C_6H_{12}O_6$) in the

presence of bacteria or yeasts emitting carbon dioxide. For this process, however, it is necessary to previously digest cellulose or starch to sugar.

A third possibility for the production of biofuels is pressing and extraction from oil crops such as rape. In principle, vegetable oils such as rape oil are suitable for operating diesel engines. Their use in modern internal combustion engines may entail disadvantages in comparison to diesel combustion, which can be avoided by transesterification of the rape oil to rape oil methyl ester. The chemical structure of e.g. rape oil is that of a fatty acid glycerol ester. If vegetable oil is converted with methanol using a catalyst (e.g. NaOH), vegetable oil methyl ester (PME) and glycerol are obtained as well as some residues [KOSSMEHL 1995], [DREIER 2000].

In order to obtain economically and energetically meaningful solutions, a holistic use of biomass should be envisaged for these production processes (e.g. fermenting and using the byproducts or gasifying the whole plants). Various pilot and demonstration projects are currently analysing the suitability of biomass for fuel production. The basic processes for the production of renewable fuels are known in principle.

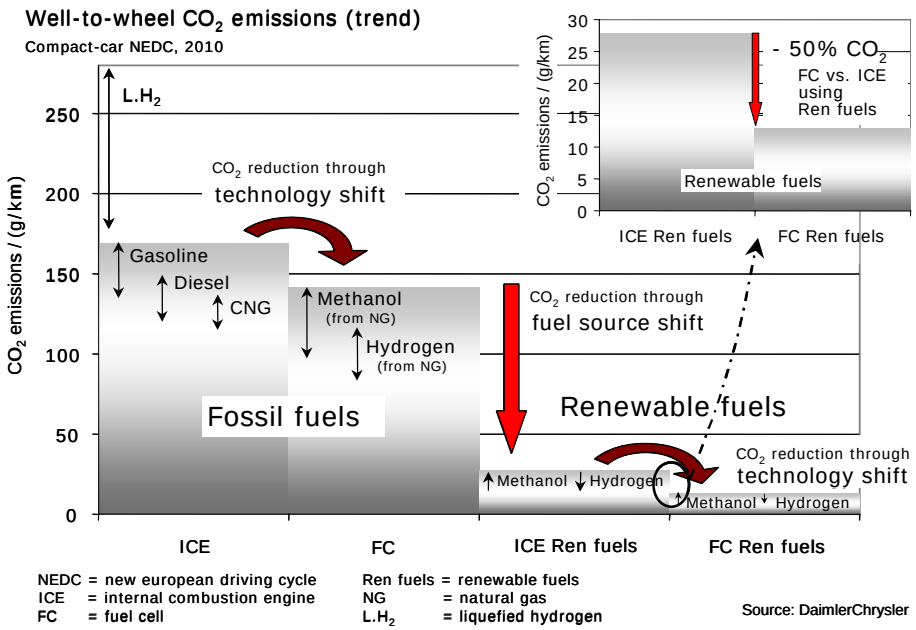


Figure 46: CO_2 reduction due to power train developments and renewable fuels

Current projects are aimed at obtaining data on energy balances, emissions and costs and evaluating optimum concepts for fuel production. These studies are necessary to match decentralized biomass procurement and corresponding processing with decentralized or centralized fuel production and obtain economically efficient solutions.

Fuels from biomass provide the possibility of making a valuable contribution to CO_2 reduction already in the medium term. More detailed investigations on this topic can also be found in the status reports of the Transport Energy Strategy [EUCAR TES 2002], in the *well-to-wheels* analysis of General Motors [GM 2002], in Isenberg/Edinger [ISENBERG EDINGER 2002] and in L-B-Systemtechnik [SCHINDLER WEINDORF 2002] as well as, in particular, in the well-to-wheel study [CONCAWE 2005].

Figure 46 illustrates possible advantages with respect to CO_2 reduction due to power train developments and changes in the fuels used. CO_2 reductions of some 10% can be achieved with advanced internal combustion engines as well as fuel cell power trains and the use of fossil fuels. Significant advantages are obtained by the use of renewable energies for fuel production. In this case, fuel cell systems can fully display their efficiency advantage.

10.3 Motivation for the use of biomass as an energy carrier

Reasons for the remarkable role of biomass in "late and post-fossil" energy scenarios are, among others:

– large globally available potential of biomass (no geographical concentration) along with storability and transportability and thus significant potential contribution to securing energy supply in the long term,
– wide range of applications (generation of heat, electricity and fuels) along with the availability of the relevant energy conversion technologies; economic efficiency in part already existing, e.g. in decentralized combined heat and power systems [ORTMAIER 2001],
– conservation of the resources of fossil energy carriers and thus in part lower dependence on oil imports (example: USA, EU, Brazil) due to the use of domestic energy carriers, new tasks for agriculture (examples: USA and EU, the latter above all in view of its recent eastward enlargement),
– contribution to environmental protection: CO_2 neutrality in use and clear CO_2 reduction in the full fuel cycle,

– use of so-called "set-aside areas" (examples: USA, EU, D) and thus possible improvement of the income situation of agriculture (substitution markets due to energy crops); new products for the agriculture of the Third World,
– beginning willingness of energy utilities to invest in renewable energies; Shell expects to produce approx. 50% of the fuels from biomass by about 2060.

10.4 Status of biogenic methanol production

The basic processes for the production of biomethanol are tested and demonstrated in laboratory experiments. Inadequately answered as yet are questions concerning quantitative statements on emission and material balances and on costs for economical fuel production:

– What energy input with corresponding emissions is necessary for the provision and conditioning as well as the processing of biomass (*input/output* analysis)?
– With what efficiency is the biomass processed to methanol (current values are in the range of 40–55%; TES: 48–56%, GM: 54%, ECOTRAFFIC: 51%)?
– At what costs will biomethanol be producible?
– How greatly centralized/decentralized must biomass provision and subsequent processing take place? Catchment areas with a radius of up to 20–25 km seem to be economically meaningful for the use of biomass.
– Can the two steps of biomass provision and processing be separated? There are solution approaches for joint processing in a decentralized plant (Prof. Th. Willner, Hamburg), for the separation of decentralized biomass processing from centralized fuel production ([WOLF RUDLOFF 2001], [WOLF 2002] and [SCHAUB 2002].

Since biomass arises locally, it is cost-intensive to collect and process it. Technical and economic solutions are needed to process biomass in decentralized, small to medium-sized gasification units, compress it energetically (bio crude oil, BCO) and transport the intermediate products to large fuel conditioning plants.

At present, various experimental facilities are being constructed and operated to answer the above questions. Finally, an answer is also to be given to the question of whether or not biogenic fuel production appears meaningful.

10.5 EU proposal for biofuel market launch

The Commission of the EU developed a proposal for a directive on the accelerated introduction of biofuels into the European fuel market. Ethanol, ETBE and methanol, which can be added to conventional fuels, as well as biodiesel, biogas, biooils and dimethyl ether were selected for market launch.

Table 33: EU target quotas in per cent for renewable and biogenic fuels

Fuels	Target year			
	2005	2010	2015	2020
Biogenic fuels	2.00	5.75	7.00	8.00
Hydrogen	0.00	0.00	2.00	5.00
Natural gas	0.00	2.00	5.00	10.00
Total	2.00	7.75	14.00	23.00
Basis: EU fuel consumption	318 [1]	338 [1]	359 [2]	379 [1]

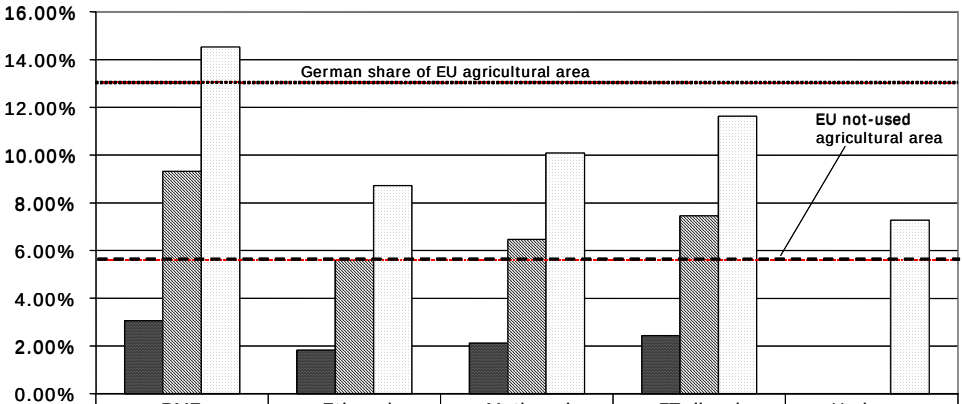
[1] million toe, after [EU 2000], [EU 2001], each set to 100% in its column; [2] interpolated

Table 33 shows the EU targets for natural gas, biofuels and hydrogen. The targets moreover include 10% natural gas to be used in the transport sector in 2020. Obligatory admixtures of renewable fuels are expected from 2008/2009 onwards. Quotas of 2% of the gasoline/diesel consumption have so far been assumed for biofuels for 2005 and thereafter an increase by 0.75 percentage points per year, so that a market share of 5.75% will be reached in 2010.

10.6 Energy crops in the EU: necessary agricultural areas

Figure 47 shows that for reaching the EU biofuel targets about 8–14% of the EU's agricultural area would have to be used for fuel production (ethanol, methanol, RME or FT diesel) up to 2020. Another 8% of the area must be reserved for hydrogen production from biomass, if hydrogen is to be provided from energy crops only. Economic evaluations will decide on whether hydrogen will be produced alternatively via electrolysis with renewable electricity. As is common practice in industry today, natural gas can also be used for hydrogen production. This production path could have

economic advantages, but would have to prove its CO_2 advantage in an overall energy evaluation.



	RME	Ethanol	Methanol	FT diesel	Hydrogen
2005	3.05%	1.83%	2.11%	2.44%	0.00%
2010	9.31%	5.58%	6.46%	7.45%	0.00%
2020	14.53%	8.71%	10.08%	11.62%	7.26%

Source: after Isenberg/Edinger in [METHANOL 2003]

Figure 47: Necessary EU agricultural area to reach the EU biofuel targets with energy crops, own calculations and [ISENBERG EDINGER 2002]

In 2002 the German agricultural area was 17,067,000 ha, the EU agricultural area 130,443,000 ha. The German set-aside area comprised 1,250,000 ha (EU: 7 million ha) and was remunerated with a set-aside premium of about 330 €/ha. The EU biofuel targets can be essentially covered by the use of set-aside areas for biomass production. In addition, wastes and residues are available for CO_2-reducing fuel production. The EU concept stipulates that no areas required for food production should be used for the cultivation of energy crops.

10.7 Biomass from waste and biogenic residues for fuel production

Residues and waste wood represent a great potential for the future production of fuels. Estimates of sustainably available quantities of wood residues from Swedish forests amount to 125 TWh/a (450 PJ/a), from Finnish forests to another 100 TWh/a (360 PJ/a) in terms of energy. In Germany up to 150 TWh/a (540 PJ/a) is annually available, which is not yet used (cf. **Table 34**).

Table 34: Technically usable potentials for biomass from waste in Germany and in the EU [KALTSCHMITT 2002], [EUCAR TES 2002]

Biomass	Germany		EU	
	TWh/a	PJ/a	TWh/a	PJ/a
Forest wood residues	85	306 100–150 1 120–230 3	834	3,000 1,800 2
Industrial timber	11	40 25–35 1		
Waste wood	25	90		
Straw	29	104 104 1 120–300 3	278	1,000 600–930 2
Total	150	540 330–620 3	1,112	4,000

1 TWh = 3.6 PJ; Sources: 1 Prognos, 2 [TUM 1998], 3 Ifeu

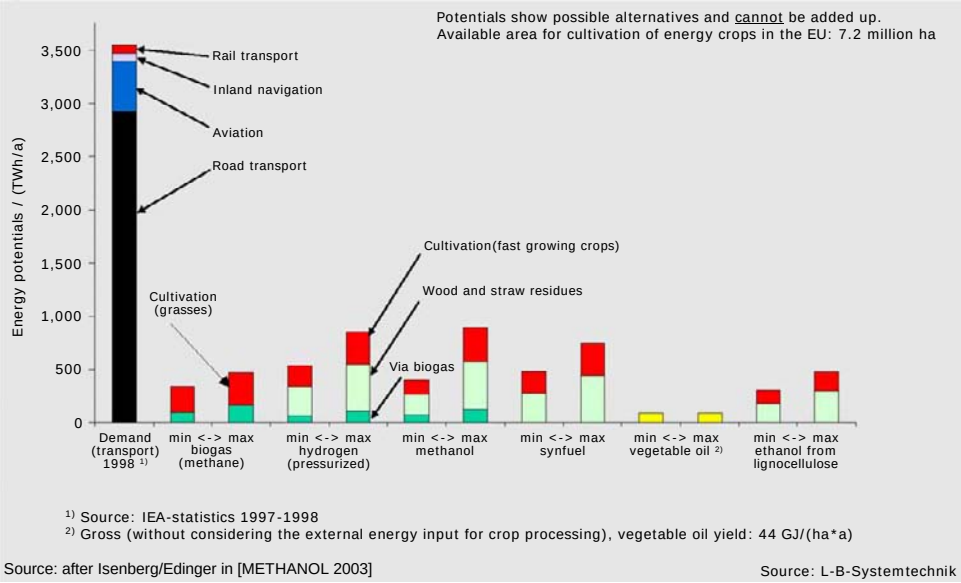


Figure 48: Possible technically usable alternative potentials for biofuels in the EU (after [SCHINDLER WEINDORF 2002])

10.8 EU resources for fuel production from renewables

Figure 48 shows technically usable potentials for biogenic fuel production in the EU15 countries. Essential fractions of biogenic fuels can be provided from wastes and residues. For energy crops a moderate use of set-aside areas was assumed (approx. 7 million ha in total). The potentials specified are not to be regarded as additive.

Sufficient renewable and biogenic resources for fuel production are thus available in order to fulfil the political goals. The Transport Energy Strategy (TES) and the *European Council for Automotive* R&D (EUCAR) estimate the potential of biogenic fuels for the EU15 countries at 15% (range 11–24%). It was assumed that 50% each of the available biomass will be used in stationary and mobile applications.

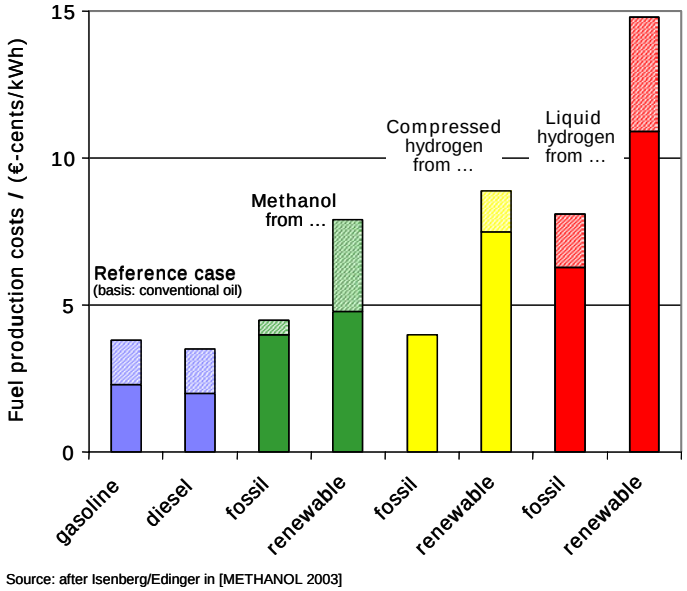
These technical potentials do not simultaneously mean economical solutions. Technological progress, economies of scale and learning curves from wind power generation and biomass gasification must show that renewable and biogenic resources may become competitive in the longer term.

10.9 Fuel production costs

The costs of fuel production are varying, depending on the primary energy carrier used. Methanol from natural gas costs about 5–7 €/GJ in production [MPE 2000] (cf. **Table 2**). Biomethanol costs up to 8 €-cents/kWh or approx. 22 €/GJ, about the same as RME without tax.

The costs for hydrogen produced from fossil and renewable sources are of the same order of magnitude, liquid hydrogen being clearly more expensive due to the comparably high energy input for liquefaction (**Figure 49**).

Large plants are likely to have clearly lower fuel production costs than small units. **Figure 50** shows cost reductions with increasing plant sizes (50–200 MW). The use of wastes and residues promises additional cost advantages over energy crops.



5 €-Cent/kWh ≈ 14 €/GJ (**Tabel 2**) ≈ 0,014 €/MJ (**Figure 2**)

Figure 49: Fuel production costs in €-cents/kWh before taxes after 2010; after [EUCAR TES 2002], DaimlerChrysler AG

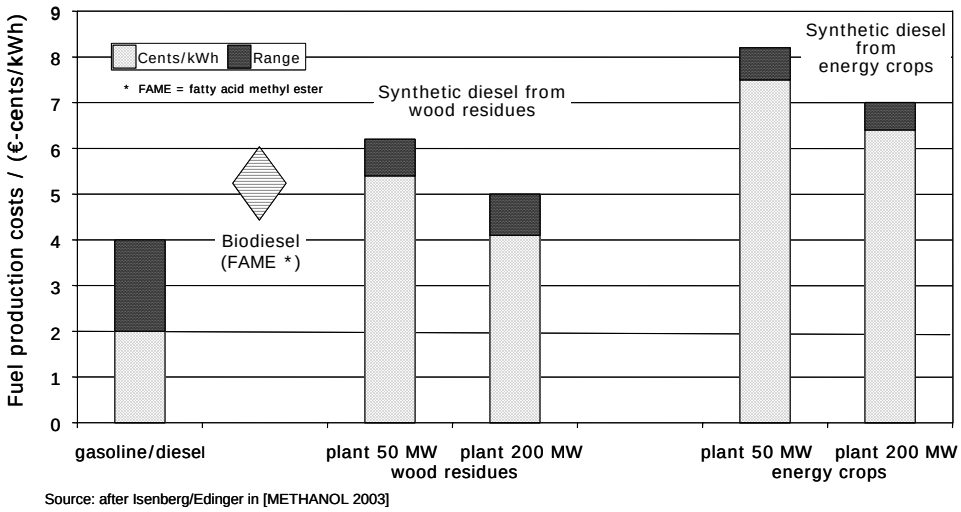


Figure 50: Fuel production costs for waste wood and energy crops in €-cents/kWh before taxes; after: [EUCAR TES 2002]

10.10 Biomass projects

Various ongoing projects are investigating the energy, technology and economic aspects of fuel production from biomass gasification and fermentation. The projects differ by the use or avoidance of intermediate energy carriers as an answer to the question of decentralized versus centralized fuel production. Up to the present, no large-scale plant for primary biogenic fuel production is in operation (but see information on the projects of the SVZ secondary raw materials exploitation company 'Schwarze Pumpe' [OBERMEIER 2001]: waste disposal and waste processing for methanol production). Methanol produced by SVZ is used in the 'Berlin Methanol Fuel Cell Project' (cf. **Chapter 11.3**).

An outstanding project has been the collaborative research project "Renewable Fuels Network of Competence" (ReFuelNet). The focus of this BMBF-funded project was on the technology development for synthesis gas production from solid biomass for subsequent fuel synthesis ([REFUELNET 2003], [REFUELNET 2005]).

At Freiberg in Saxony, CHOREN Industries together with its partners DaimlerChrysler AG and Volkswagen AG investigate the gasification of wood residues for a subsequent Fischer-Tropsch process. By means of the Carbo-V® process CHOREN successfully demonstrated the gasification of biogenic residues and the conversion into synthesis gas. Methanol or Fischer-Tropsch diesel have been optionally produced in the fuel synthesis stage (**Figure 51**). The adaptation of biomass gasification to the requirements of fuel synthesis demonstrated the process engineering for the production of biogenic fuels.

At present, a substantially larger plant is being constructed. Its target is the conversion of 65,000 tons per year of dry biomass into 17.8 million litres of liquid fuel. The plant is intended to go into operation by 2007. Subsequently, five plants are planned at five different sites all over Germany with an individual biomass input of about 1 million tons per year of dry biomass in the mid-term [SCHULZE RUDLOFF 2006].

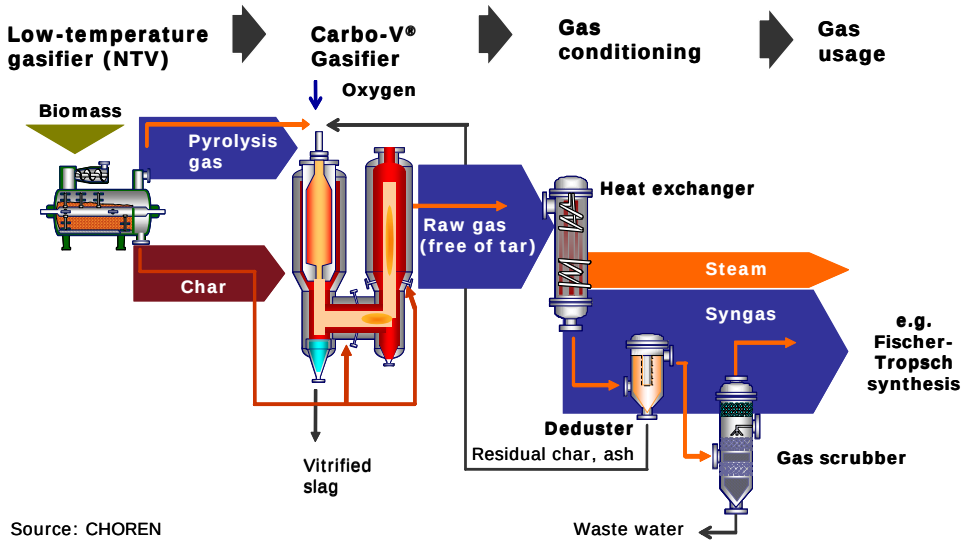


Figure 51: The Carbo-V® process for the conversion of solid biomass feedstocks into a synthesis gas for fuels production (Source: CHOREN)

10.11 Summary of Chapter 10

The investigations show that there are sufficient potentials available to reach the EU target of 8% biofuel in 2020. Various ongoing projects are investigating the energy, technology and economic aspects of fuel production from synthesis gas. The projects differ by their primary products and energy management especially with respect to the secondary energy carriers, final energy carriers and byproducts. An essential task today is to provide verifiable data by relevant energy, material and cost balances (including life cycle assessments) in order to improve the informative value of the study comparisons shown. Political boundary conditions must be revised.

11 Special aspects

11.1 Fuel cells for portable applications

Portable applications with grid-independent energy supply include above all emergency power-generating units (premium power, uninterruptible power systems, UPS) for medical facilities and rescue services, alarm and warning systems and telecommunications; added to this are mobile phones and portable computers, camcorders, devices for container and waggon tracing, site determination devices, leisure and camping equipment [STOLTEN et al. 2002]. Self-contained power supplies also included auxiliary power units (APUs), which can be operated independently of the drive unit of a vehicle.

The relatively short half-life of mobile electronic appliances with respect to the latest state of the art and their short service life opens up the possibility of equipping new generations of devices faster with novel electric power generators [PEHNT 2002]. The most important criteria are energy density, operating life, charging/replacement time and storage volume [SFC 2003].

These criteria are fulfilled, for example, by small fuel cells. They fit in small devices confined in space, have an acceptable weight and increase the grid-independent operating time. Only the storage unit of the energy carrier must be replaced. Candidates for small devices are low-temperature fuel cells such as PEFCs and DMFCs, whereas APUs may require high-temperature fuel cells such as the SOFC.

PEFCs can be operated with pure hydrogen from liquid-, pressure-, hydride- or carbon-based storage units or with hydrogen from the reforming of liquid energy carriers. For portable small devices, reforming appeared not mature enough just a few years ago. In contrast, direct electricity generation from alcohols in fuel cells suggested itself, e.g. methanol in direct methanol fuel cells [OERTEL FLEISCHER 2001]. However, development is still needed and possible for the DMFC concerning its performance characteristics, efficiency, production costs and service life. The performance target is to compete with lithium/ion batteries. The computer manufacturer CASIO holds the view today that DMFCs cannot be applied – for example, in laptops – before they have demonstrated sufficient power density. Until then, a modified low-temperature fuel cell type will be preferred whose hydrogen demand is to be covered from the reforming of

methanol ([FCTD 2003], [FCWRK 2003]). Besides PEFCs and DMFCs, other fuel cells and other energy carriers (e.g. diesel or kerosene [SFC 2003]) with and without reformer are also conceivable. The aim of developments is micro fuel cells and micro-reformers.

11.2 Ban on MTBE

Since 1979, MTBE has been used nationwide at low admixture levels in gasoline to replace lead as an octane booster or anti-knocking agent. Public Law 101–549 (Clean Air Act Amendments of 1990) established a fuel oxygenate standard according to which reformulated gasoline must contain at least 2wt% oxygen and the fuel industry responded to the fuel oxygenate standard by making substantial investments in MTBE production capacity and systems to deliver MTBE-containing gasoline to the market (sec. 1502) [ENERGY ACT 2005].

Because of the hazard potential of MTBE nationwide either a partial or a complete ban was placed on MTBE. In the State of California (EPA region 9 [19]), the admixture of MTBE to reformulated gasoline has been prohibited since 1/1/2004 [CAGOV 2002]. In the meantime, less than half of the states have phased out MTBE except the states of Maine and New Hampshire (EPA region 1): the phase-out date of their partial ban was fixed on 1/1/2007 [EPA 2004].

The phase-out of MTBE has led to a large decrease of MTBE imports from East Asia and the Middle East. Exports to the U.S. have declined by about 47% (850,000 tons) since 2001. But this volume seems to be needed in view of the growing demand in Asia because of lead phase-out and growth in gasoline consumption [SHIR 2005].

Ethanol is considered to be the leading oxygen donor for the replacement of methanol [20]. Due to the lower molar mass of ethanol in comparison to MTBE, however, the replacement of MTBE by ethanol – providing the minimum oxygen content – leads to a reduction in volume and reduces

[19] In the context of fuel supply (e.g. reformulated gasoline, MTBE) special US regions or states are often referred to as *PADDs*. In case of environmental problems another classification is used, the *EPA region* (cf. **Chapter 14.2.2**).

[20] Concerning the volatility of MTBE and ethanol from water cf. Henry coefficient (**Table 26**).

the octane number of the reformulated gasoline. In addition, air pollutant emissions (VOC, MSAT, NOx) are increasing. As a consequence of a ban on MTBE, the mentioned losses and emission disadvantages have to be compensated by modifying the design of the reformulated gasoline via production changes in the refinery processes and by additional measures.

Both the ban on MTBE and the introduction of ethanol (from corn) as a possible substitute or a fuel have been discussed nationwide by the different interest groups in the USA [EIA 2002], [MI 2003], [PATZEK 2003], [BLUEBOOK 2003].

On 8/8/2005 the U.S. Energy Bill (Energy Policy Act of 2005 / HR6) was adopted and signed into law by President Bush. This did not ban MTBE at the federal level. In order not to filibuster the bill, as was done in 2003, among other items the MTBE liability waiver was not included (shielding the companies responsible for MTBE contamination from their full financial liability for the damage they have caused). These issues will be pursued in separate initiatives [EWALL 2005]. A provision to move MTBE lawsuits from state courts to federal courts remained in the bill (sec. 1503) and the elimination of the oxygen content requirement for reformulated gasoline was included (sec. 1504) [ENERGY ACT 2005].

11.3 Berlin methanol fuel cell project [21]

On 30 September 2004, Bewag AG – together with the partners Vattenfall Europe, E.ON Energie and the manufacturer MTU CFC Solutions – put the first methanol-operated high-temperature fuel cell worldwide into operation in its heating plant in Berlin-Treptow. Methanol can be produced from various biomass products and residues and is considered to be one of the options of the future for the energy market. A prerequisite for efficient utilization as an energy carrier is the use in energy conversion systems with high efficiency, such as fuel cells. The technology of the MCFC (molten carbonate fuel cell) is regarded as pioneering. The project is therefore financially supported by the Federal Ministry of Economics and Labour.

The project aims at testing this new technology under practical conditions. For this purpose, the fuel cell system will be operated for several years in conjunction with the existing electricity and heat supply units. The methanol needed for operation comes from the secondary raw materials exploi-

[21] Chapter 11.3 sources: figures after Pokojski/Radke (BEWAG/Vattenfall), 2005.

tation company (SVZ) “Schwarze Pumpe”, where it is produced from waste and biomass (cf. **Chapter 10.10**).

MCFCs working at temperatures between 500°C and 650°C are being developed for industrial applications. They permit electricity generation with high efficiencies (approx. 55%) and the simultaneous production of process steam, offering an excellent potential for industrial combined heat and power generation. The electrolyte of this high-temperature fuel cell consists of carbonate salts, which are liquid above a temperature of about 450 °C.

The MCFC developed by MTU CFC was designed for the use of natural gas. It consists of the units Media Supply, Hot Module, inverter and the associated control unit. The Media Supply contains the component for water treatment, an activated carbon filter, HUMIHEX (humidifying heat exchanger) and the prereformer and serves to supply the fuel and consumables and to process the consumables for use in the Hot Module. The Hot Module containing the fuel cell is regarded as the heart of the plant. It produces electricity and heat from the fuels. The inverter transforms the direct voltage produced into alternating voltage. The control unit serves to control and regulate the overall system. A heat exchanger permits the waste heat to be used for heating purposes.

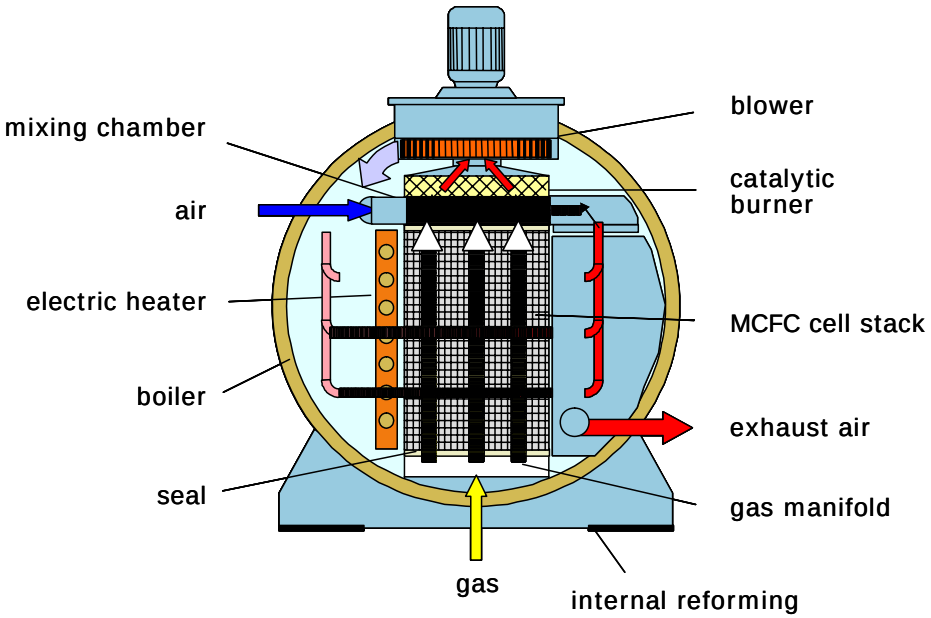


Figure 52: MCFC Hot Module (internal reforming)

A characteristic feature of the MCFC system is the reforming of methane-containing (CH_4) fuels inside the fuel cell. Natural gas or other biogases can be directly reformed into a hydrogen-rich feed gas in the fuel cell after desulphurization by means of an activated carbon filter, enrichment with steam and prereforming (splitting of longer hydrocarbon chains) and converted into electricity and heat in a second step. The process gas is passed for this purpose through the fuel cell via a U-shaped tube bundle and converted into a hydrogen-rich gas with the aid of a catalyst. Since fuel reforming takes place directly in the fuel cell, one speaks of internal reforming. Upstream gas treatment, as is usual for low-temperature technologies, is not needed (**Figure 52**).

Apart from natural gas, the system can also be operated with methanol. In bivalent operation, the natural gas/methanol mixing ratio can be continuously varied between 0 and 100%. The mode of operation can thus be optimized at any time from cost and process-engineering aspects.

The use of methanol (CH_3OH) changes the reforming process in the fuel cell. In contrast to methane, which reacts endothermically during reforming in the MCFC, the reaction is exothermic in the case of methanol, so that a temperature increase in the fuel cell must be assumed, which requires precooling and a conversion of the methanol into methane and water in a prereforming step.

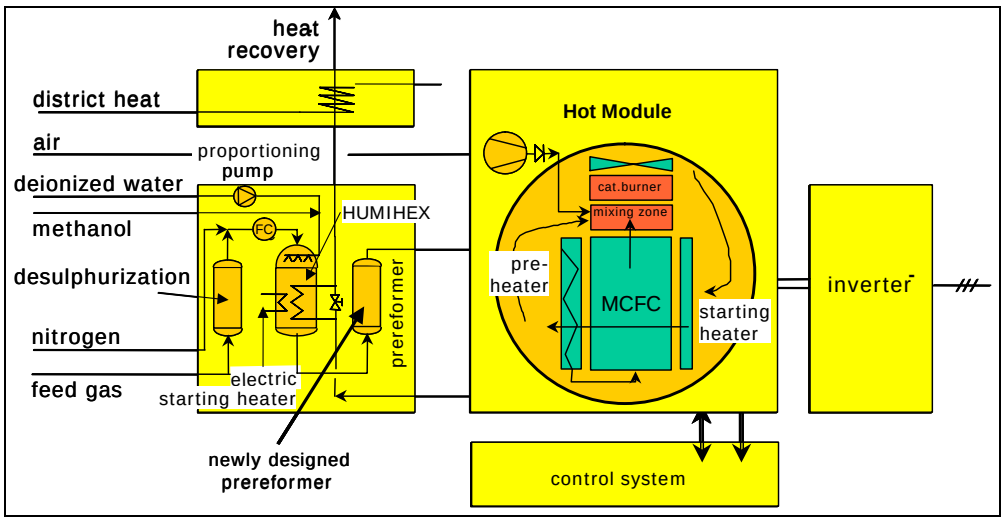


Figure 53: Components of the MCFC system for methanol operation

For this reason, a new air-cooled prereformer has been developed. As a tubular heat exchanger it ensures sufficient cooling of the feed gas at any time and makes it possible to largely convert the methanol into methane and water.

In addition to the existing Media Supply, a methanol rack has been provided, which contains all the components additionally required – new prereformer, fresh air fan and exhaust air system. Methanol is supplied by the HUMIHEX (**Figure 53**).

The system has an electrical power output of 220 kW and a thermal power output of approx. 170 kW. The electrical net efficiency is in the range of 45% at full load, the overall efficiency including heat recovery is roughly 80%.

The costs of the project planned for three years amount to roughly 4.5 million €. About 2 million € is borne by the Federal Ministry of Economics and Labour. The remaining costs are shared between the project partners Vattenfall Europe and E.ON.

11.4 Summary of Chapter 11

The most important criteria for portable applications of fuel cells are energy density, operating life, charging/replacement time and storage volume. Candidates in the low-temperature range are PEFC and DMFC. Pure hydrogen or hydrogen from the reforming of liquid energy carriers can be used as the fuel. Further development for the fuel cells is still needed. The performance target is to compete with lithium/ion batteries. The aim of developments are micro fuel cells and micro-reformers.

Less than half of the states have phased out MTBE. The U.S. Energy Bill of 8/8/2005 did not ban MTBE at the federal level. This issue will be pursued. A provision to move MTBE lawsuits from state courts to federal courts remained in the bill and the elimination of the oxygen content requirement for reformulated gasoline was included.

Aim of the Berlin project is testing the methanol-operated high-temperature fuel cell under practical conditions. The MCFC which was designed for the use of natural gas has been modified with a new air-cooled prereformer in a methanol rack. Thereby the system can be operated with natural gas and/or methanol in a bivalent manner.

12 Summary

In the medium- to long-term perspective, new final energy carriers for vehicles will be produced on a fossil and increasingly on a renewable basis and will play a part in the energy market. In order to utilize them, in addition to further developed internal combustion engines, hybrid vehicles and electrically driven fuel cell vehicles will also have to be taken into consideration in future.

Methanol as an energy carrier can make an essential contribution here. Methanol can be used in an environmentally friendly manner in gasoline/methanol mixtures for flexible fuel vehicles with internal combustion engines and in diesel engines with pure methanol. Furthermore, it can be used in fuel cell vehicles with on-board hydrogen production, directly in direct methanol fuel cell drives and in stationary systems for electricity and heat generation. Finally, in portable applications it serves as an energy carrier for electric power generators.

Methanol can be produced both from fossil energy sources – today mainly from natural gas for the chemicals market – and from biomass or waste materials through the process steps of synthesis gas generation with subsequent methanol synthesis. In this connection, the low-cost remote or stranded natural gas plays a particular role, which can be converted into methanol as an energy carrier or chemical feedstock far away from the markets and from a pipeline infrastructure and then transported to the consumers. For the fuel supply in the European Union (EU) 3% methanol can already be used today as an additive to gasoline. Since 2005 an EU directive for fuels on a renewable basis has required a share of at first 2% in total fuel supplies.

At the filling station, the costs of providing methanol as an energy carrier based on low-cost natural gas could only be insignificantly higher than for gasoline/diesel before tax under the present boundary conditions. Moreover, methanol is a liquid energy carrier like gasoline/diesel fuel which we are used to handle today and has a storage density of about 50% of that for gasoline/diesel refuelling systems; but it is clearly higher than that of hydrogen refuelling systems. If used in accordance with regulations and if all relevant rules are observed, handling methanol does not represent any health or safety problem.

Methanol can also be used to produce other fuels such as hydrogen, dimethyl ether or synthetic gasoline or diesel. The latter can also be co-

produced with propylene for the plastics market, in particular on the basis of low-cost large natural gas deposits and associated gas far away from all pipeline systems.

In this book, the processes for the production and use of methanol are presented and evaluated, markets and future options discussed and issues of safety and environmental impacts addressed with the following messages.

Methanol as an **option for the energy market** should be maintained because it is currently impossible to decide on future new energy carriers for road traffic; all relevant development approaches should be further pursued.

Feasible concepts for vehicles with methanol, reformer, fuel cell and electric drive still have to undergo a further development phase with respect to cost reduction and technical performance. In the long run, the use of methanol in direct methanol fuel cells (DMFCs) for vehicle drives could play a key role; DMFCs are being developed and tested today for portable and light traction applications.

Methanol production is chiefly based on natural gas today, in Germany also on residual oils. The production of methanol on the basis of input materials other than natural gas (e.g. coal or residual oils) is more complex in terms of process engineering.

Methanol use today takes mainly place in the chemical industry. In the EU methanol can be used as a gasoline additive; it is also used for MTBE production in the EU.

Methanol prices today will be greatly influenced by the price of natural gas. The ban on the use of MTBE especially in California and in many other US states, the growing demand of MTBE in Asia on the one hand, and the enhanced use of inexpensive associated gas for the production of methanol in so-called megaplants, on the other, will have severe implications for the future methanol market.

Future **methanol markets** for road traffic cannot be defined at present. If additional production capacities should be required in the future, their selection should be made from the aspect of a methanol provision that is ecologically justifiable and competitive on the energy market. Furthermore, a fiscal policy not in sight today would have to support the boundary conditions for the introduction of new energy carriers in road traffic.

Investments in increasingly larger **methanol plants** are being made but it could be possible that new capacity not all expected will become com-

mercial and available for the market. All the new production facilities produce methanol where the gas deposit is located and they have favourable gas conditions in the long term. But none of these facilities will suffice to produce and supply the quantities required if syngas/methanol were to play an increasing role as a new energy source for road traffic one day.

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14 Annex

14.1 Supplementary tables

Table 35: Compilation of the Lurgi processes mentioned here

Conversion / explanation	Process
Autothermal + steam-reforming	Combined Reforming
Conversion of olefins to diesel	COD
Gas to chemicals	GTC®
Gasification of coal	BG-Slagger-Process
Methanol to DME	MTD, Mega DME
Methanol to gasoline	MTG
Methanol to hydrogen	MTH®
Methanol to propylene	MTP®
Methanol to synthetic fuels	MtSynfuels®
Methanol/DME to power (electricity)	MtPower®
Natural gas to methanol	MegaMethanol®
Two-stage methanol synthesis	Combined Converter Methanol Synthesis

Table 36: Henry coefficients for some substances

Substance	Henry coefficient [1]	Sources [2]
Benzene	0.227	[SCHROEDER 2002], [SANDER 1999]
ETBE	0.11	[HALLBERG 2001]
Ethanol	0.000213	[SCHROEDER 2002], [SANDER 1999]
Ethanol	0.00025	[HALLBERG 2001]
Methanol	0.000186	[SCHROEDER 2002], [SANDER 1999]
MTBE	0.033	[SCHROEDER 2002], [EWEIS 2000]
MTBE	0.02–0.12	[LINNEMANN 2003], [SQUILLACE 1997]
MTBE	0.018	[HALLBERG 2001]

[1] at 25°C; [2] [source_B], [source_A]: [source_B] was used here; but the primary literature is [source_A] cited in [source_B]

Table 37: CO_2 balances for different processes for the production of energy carriers

Production process for the *ENERGY CARRIER*	Specific CO_2 emissions [1] / (kg_{CO2} / GJ_{EC}) [3]	Thermal efficiency [1] / %
METHANOL from natural gas	16	67
METHANOL from hard coal (autothermal)	142	45
METHANOL from hard coal (allothermal with nuclear high-temperature reactor / HTR)	53	38
METHANOL from lignite (North Dakota)	116	48
METHANOL from residual oil	38	56
DME from natural gas	16	66
HYDROGEN from methanol (from natural gas)	76 (92)	89 (60)
FTD from natural gas	n.d. [2]	~60
DIESEL from methanol (from natural gas)	n.d. [2]	~65

[1] Basis: lower heating value LHV; after [HÖHLEIN et al. 1995] and LURGI;
[2] = no data available; [3] EC = energy carrier

Table 38: Lower heating values and specific densities of some energy carriers

Energy carrier	Lower heating value /		Density ρ / (kg/m^3)
	(MJ/kg)	(MJ/dm^3)	
Diesel fuel	43	36	840
DME	28	19	666
Ethanol	27	21	789
LPG	46	25	540
Methanol	20	16	791
MTBE	35	26	740
Gasoline fuel regular gasoline	52–39 40	33 30	630–830 748
Rape oil (crude)	37	34	916
RME	37	33	882
Hydrogen	120	0.011	0.09

Substance values at approx. 1 bar/15°C, after various sources; rounded

14.2 Abbreviations, explanations, conversions

14.2.1 Abbreviations

ATR	autothermal reforming
barg	bar – gauge (above atmospheric pressure)
bbl	barrel
BCO	bio crude oil
BFW	boiler feed water
bpd	barrel per day (bbl/d)
Btu	British thermal unit
$C.H_2$	compressed hydrogen
CAS	chemical abstracts service
CIS	Commonwealth of Independent States
C.MG	compressed methane gas (by fermentation of biomass)
C.NG	compressed natural gas
CAA	Clean Air Act (US legislation)
CaFCP	California Fuel Cell Partnership
capex	capital expenditure (process capital costs)
CC	combined cycle
CCS	carbon capture and sequestration (storage)
CGH_2	compressed gaseous hydrogen (C.H2)
C_nH_m	hydrocarbons
CPO	catalytic partial oxidation
DI engines	direct-injection engines
DME	dimethyl ether
DMFC	direct methanol fuel cell
DMT	dimethyl terephthalate
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EFTA	European Free Trade Association
EPA	Environmental Protection Agency (USA)
EPC	engineering, procurement and construction (contract) (cf. turn-key)
ETBE	ethyl tert-butyl ether

EU15	European Union with 15 member states
EUCAR	European Council for Automotive R&D
EXAFS	extended X-ray absorption fine structure
FAME	fatty acid methyl ester (biodiesel)
FC	fuel cell
FFC	full fuel cycle
FFV	flexible fuel vehicle
FOB	free on board (Rotterdam)
FT	Fischer-Tropsch (synthesis)
FT-d	Fischer-Tropsch diesel
GNP	gross national product
GT	gas turbine
GTL	gas-to-liquids (conversion process for gaseous to liquid energy carriers)
HHV	higher heating value (basis)
HMI	Hahn-Meitner Institute
HTFC	high-temperature fuel cell
HTAS	Haldor Topsøe A/S
HTS	high temperature shift (reactor)
ICE	internal combustion engine
IGCC	integrated gasification combined cycle
IR	infrared
$L.H_2$	liquid hydrogen
LHV	lower heating value
LNG	liquified natural gas
LPG	liquified petroleum gas (propane/butane mixture)
LTFC	low-temperature fuel cell
LTS	low-temperature shift (reactor)
M100	fuel with 100% methanol
M15	fuel with 15% methanol + 85% gasoline
M85	fuel with 85% methanol + 15% gasoline
MEK	methyl ethyl ketones
MeOH	methanol
MFC	multi-fuel concept

MFCA	Methanol Fuel Cell Alliance
MFV	multi-fuel vehicle
MMA	methyl methacrylate
MON	motor octane number
MSAT	mobile source air toxics
MT	metric tons
MTBE	methyl tert-butyl ether
MTG	methanol to gasoline
MTO	methanol to olefins
MTPD	metric tons per day
NG	natural gas
NHE	normal hydrogen electrode
NMHC	non-methane hydrocarbons (without solvent)
NMOG	non-methane organic gases
NO_x	nitrogen oxide
opex	operating expenditure (process operating costs)
PADD	petroleum administration for defense district
PEFC	polymer electrolyte fuel cell (fuel cell with a polymer membrane as the electrolyte)
PET	polyethylene terephthalate
PME	palm (oil) methyl ester
POX	partial oxidation
PSA	pressure swing adsorption
psi	pounds per square inch
PZEV	partial zero-emission vehicle (US/CA standard)
RME	rape (oil) methyl ester
ROI	return on investment
RON	research octane number
RVP	Reid vapour pressure
S/C	steam to carbon (ratio)
SAPO	silicoaluminophosphate catalysts
SMR	steam methane reformer / reforming
SNG	substitute natural gas
SOFC	solid oxide fuel cell (HTFC with solid electrolyte)

synfuel	synthetic fuel
SunFuel®	synthetic fuel on the basis of regenerative biomass (® trademark of Volkswagen AG)
syngas	synthesis gas
tce	tons of coal equivalent
TDS	thermal desorption spectroscopy
TEM	transmission electron microscopy
TES	Transport Energy Strategy
TIGAS	Topsøe integrated methanol/DME and gasoline synthesis
toe	tons of oil equivalent
TPD	temperature-programmed desorption
UHV	ultra-high vacuum
ZEV	zero-emission vehicle (US/CA standard)

14.2.2 Definitions / explanations

alkanes
: saturated acyclic hydrocarbons (C_nH_{2n+2})

alkenes
: unsaturated acyclic hydrocarbons (C_nH_{2n})

APU
: auxiliary power unit (power supply that is independent of the drive unit of a vehicle; electric power generator (e.g.) with HTFC and diesel fuel)

ARA area
: natural gas; Antwerp, Rotterdam, Amsterdam; delivery place Rotterdam; trading place and hub / interconnector: Zeebrugge/B

associated gas
: gas produced in oil extraction; may be vented or flared

blend
: addition/admixture

carbon conversion rate
: the ratio of the number of produced moles of CH_3OH to the number of consumed moles ($CO + CO_2$)

catalytic conversion
: water-gas shift reaction

cetane number
: measure of the ignition quality of fuels for diesel engines

combined cycle (CC):
: a gas turbine (GT) in a power station is used to generate electricity, and the waste heat from the GT is used to produce steam to generate additional electricity via a steam turbine

converter feed
: the mixture of make-up gas and recycle gas.

dehydrogenation
: extracting hydrogens (from a chemical compound)

E5
: ethanol as a blend component

EPA Region
: Classification of US states and territories into 10 regions [EPA 2006]
Region 1: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont.
Region 2: Commonwealth of Puerto Rico, New Jersey, New York, U.S. Virgin Islands.
Region 3: Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, West Virginia.
Region 4: Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee.
Region 5: Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin.
Region 6: Arkansas, Louisiana, New Mexico, Oklahoma, Texas.
Region 7: Iowa, Kansas, Missouri, Nebraska.
Region 8: Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming.
Region 9: American Samoa, Arizona, California, Commonwealth of the Northern Mariana Islands,Guam, Hawaii, Nevada.
Region 10: Alaska, Idaho, Oregon, Washington.

EU15

15 member states of the European Union (up to 2003): Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain, Sweden, United Kingdom.

EU25

EU15 +10 new EU candidate countries (from 2004): Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovakia, Slovenia

European Free Trade Association (EFTA)

7 EFTA member states (up to 1995): Austria, Finland, Iceland, Liechtenstein, Norway, Sweden, Switzerland. 4 EFTA member states (from 1995): Iceland, Liechtenstein, Norway, Switzerland (non-EU members), 3 member states to the EU (from 1995): Austria, Finland, Sweden

FFC

full fuel cycle from primary energy carrier to end use

flaring of natural gas:

natural gas typically associated at oil fields

grade AA methanol

cf. **Table 8**

green field

natural gas (well) – methanol production (balance ± 0) – ship

heavy feedstock

cf. heavy natural gas

heavy natural gas

natural gas with high content of higher hydrocarbons

Henry coefficient

dimensionless quotient of the molar concentration in the gas and water phase; strictly speaking, only applies to substances with low water solubility and ideal behaviour in the sense of the gas laws; in ecochemistry, measure of the volatility of a chemical from water at a given temperature [ROEMPP 2003] (examples cf. **Table 24**).

HTER

Haldor Topsøe Exchanger Reformer; installation in parallel (-p) or series (-s) with the autothermal reformer

hub
: grid node; here: for natural gas pipelines

integrated gasification combined cycle (IGCC):
: the GT in a CC power station is fired on a gas fuel derived from the gasification of liquid or solid carbonaceous materials

interconnector
: natural gas pipeline between the European Continent (Zeebrugge/B) and the British Isles (Bacton/England)

light feedstock
: cf. light natural gas

light natural gas
: natural gas with low content of higher hydrocarbons

low grade methanol
: cf. **Table 8**

M3
: methanol as a blend component (gasoline blend)

make-up gas
: the synthesis gas passing from the synthesis gas preparation section to the synthesis loop

Methanol-to-Shift™
: Haldor Topsoe AS trademark

module M
: the methanol synthesis gas is characterised by the stoichiometric ratio M = $(H_2-CO_2)/(CO+CO_2)$

naphtha
: special petroleum / petroleum fractions in cracking and distillation; most important raw material source in petrochemistry

octane number
: measure of the anti-knock properties of fuels for gasoline engines

olefins
: alkenes

PADD
: Classification of US states into 5 districts (definition since World War II) [EIA 2004]

PADD 1: Connecticut, Delaware, District of Columbia, Florida, Georgia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, North Carolina, Pennsylvania, Rhode Island, South Carolina, Vermont, Virginia, West Virginia.
PADD 2: Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Oklahoma, South Dakota, Tennessee, Wisconsin.
PADD 3: Alabama, Arkansas, Louisiana, Mississippi, New Mexico, Texas
PADD 4: Colorado, Idaho, Montana, Utah, Wyoming
PADD 5: Alaska, Arizona, California, Hawaii, Nevada, Oregon, Washington

premium power
: highest-quality power supply

purge gas
: the gas withdrawn from the synthesis loop to remove excess reactants (mainly hydrogen) and to prevent build-up of inerts (mainly methane, nitrogen, and argon).

recycle gas
: the gas which is returned to the synthesis reactor after separation of raw product in the product separator

reformulated gasoline
: "improved" gasoline; free of sulphur; with MTBE addition; not precisely defined, modified compositions (USA); purpose: reduction of pollutant emissions

Reid vapour pressure
: standardized measuring procedure in the USA for the vapour pressure of a liquid; in pounds per square inch (psi) at 100 °F

remote gas
: (also: stranded gas); gas deposit too remote; transport as gas uneconomical; accounts for 80% of worldwide proven reserves [IAEE 2003] (cf. also: Oil, Gas and Energy/OGEL; http://www.gasandoil. com)

reserves
: developed energy carrier deposits

resources
: non-developed energy carrier deposits

sequestration
: selective separation of CO_2 and long-term storage (of carbon)

stranded gas
: cf. remote gas

stranded natural gas
: natural gas at remote locations

teratogenic
: effects causing malformations

turn-key
: the supplier must construct and hand over the complete plant ready for operation. All supplies and services belong to his scope of work. He guarantees completion according to schedule and warrants the quality. Within these limits he is relatively free.

UPS
: uninterruptible power supply

well-to-wheels analyses
: balance of full fuel cycle (FFC) and emission chains (CO_2) for passenger car operation including fuel supply

14.2.3 Chemical compounds

acetic acid (CH_3COOH, $C_2H_4O_2$)

carbon dioxide (CO_2)

carbon monoxide (CO)

diesel fuel (~ $C_{13}H_{24}$, [ROEMPP 2003])

dimethyl ether (H_3COH_3C, C_2H_6O)

dimethyl terephthalate, DMT (CH_3O-CO-C_6H_4-$COOCH_3$, $C_{10}H_{10}O_4$)

ethanol (C_2H_5OH, C_2H_6O)

ethyl tert-butyl ether, ETBE ($C_6H_{14}O$)

formaldehyde (CHOH, CH_2O)

formic acid (HCOOH, CH_2O_2)

glycerol (CH_2OH-CHOH-CH_2OH, $C_3H_8O_3$).

hydrogen (H_2)

isobutene (C_4H_8)
methane (CH_4)
methanol (CH_3OH, CH_4O)
methyl methacrylate, MMA ($CH_2C(CH_3)CO_2CH_3$, $C_5H_8O_2$)
methyl tert-butyl ether, MTBE ($C_5H_{12}O$)
polyethylene terephthalate, PET $(C_{10}H_8O_4)n$
rape oil (~ $C_{57}H_{101.6}O_6$, [ROEMPP 2003])
rape oil methyl ester (~ $C_{19}H_{35.2}O_2$, [ROEMPP 2003])

14.2.4 Specification of quantities

1 million = 10^6
1 t/d = 1 ton per day
1 t/y = 1 ton per year
ppmv = ppm (volume)
ppmw = ppm (weight, mass)

14.2.5 Conversion of units

1 bar = 10^5 Pa
1 bbl = 158.9873 litres
1 GJ = (100/0.36) kWh
1 mbar = 1 hPa
10 mbar = 1 kPa
1 million tce = 29.308 PJ (LHV)
1 MMBtu = 1.055056 GJ
1 psi = 6.89476 kPa
1 toe = 41.868 GJ (LHV)
t/°F = (t/°C ∗ 1.8) + 32

14.2.6 Estimation of units

1 MMBtu ≈ 1 GJ
1 US$ ≈ 1 € (mid-2003)
1 US$/MMBtu ≈ 1 €/GJ

15 Keywords

Schriften des Forschungszentrums Jülich
Reihe Energietechnik / Energy Technology

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   Proceedings of the Seventh European Fusion Theory Conference
   edited by A. Rogister (1998); X, 306 pages
   ISBN: 3-89336-219-3

2. **Radioactive Waste Products 1997**
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3. **Energieforschung 1998**
   Vorlesungsmanuskripte des 4. Ferienkurs „Energieforschung“
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   ISBN: 3-89336-258-4

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    edited by K. Hilpert, F. W. Froben, L. Singheiser (2000), 292 pages
    ISBN: 3-89336-259-2

11. **Investigation of the Effectiveness of Innovative Passive Safety Systems for Boiling Water Reactors**
    edited by E. F. Hicken, K. Verfondern (2000), X, 287 pages
    ISBN: 3-89336-263-0

12. **Zukunft unserer Energieversorgung**
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    Annex X. Final Report 1997 - 1999
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