especially equipped with atmospheric burners for combustion of landfill gases. Each boiler has its own individual water cycle and feeds into the hot water tank.

The *hot water storage* consists of 2 isolated cylindrical tanks, which function according to thermal stratification, and are placed in series. The storage volume is 8 m^3, and the temperature between 60 and 130 °C. The tanks are connected to a pressure equalizing tank.

Hot water distribution consists of fixed and flexible isolated pipes (heat transfer coefficient of polyurethanfoam isolation at 20 °C: 0.084 kJ/mh °C)[16], of hot water pumps and additional pressure regulators. The flexible pipes to the consumers are put under ground. A part of the hot water produced is used directly for the operation of the landfill heating and sanitary installations, while the rest is transported to private consumers. Heat exchangers are installed between the hot water cycle and the consumers for operational safety reasons. In order to ensure independence of consumers during disturbances, the heat exchangers are installed parallel to the existing heating plant. If the hot water supply cuts out, the heating plant of the consumer starts functioning automatically.

Costs

Based on the data obtained from the Croglio sanitary landfill, several cost aspects are given below to show the amount of investment required for a plant which can function economically if hot water consumers are in the immediate vicinity.

Investments (including salaries)	
Burners and boilers (pipes 335 MJ/h)	SFr. 15,000.-
Hot water storage (2 tanks with a 3-m^3 content)	SFr. 11,000.-
Installations for heat transport (pipe lines, circulating pumps, valves, etc.)	SFr. 6,000.-
Underground pipes to the consumers (flexwell-pipes 30 m each way)	SFr. 10,000.-
Additional installations at the consumer (heat exchanger, boiler, electrical controls)	SFr. 15,500.-
Miscellaneous (costs for planning, etc.)	SFr. 7,500.-
Total investments	SFr. 65,000.-
Revenues	
Savings at the landfill operation itself by the conversion from electricity to landfill gas combustion for the production of hot water	SFr./y 8,000.-
Estimated energy supply to the consumers (introduction price)	SFr./y 1,570.-
Total revenues and savings respectively	SFr./y 9,570.-
Amortization	
Yearly amortization of 6% interest in 10 years	SFr./y 8,450.-

Experiences with the plant

The mentioned plant has been operating automatically since November 1979 without failures. The daily methane consumption is presently 150 m^3, and the estimated efficiency is around 0.6.

---

* Authors' addresses: M. Gandolla, Dipl. Ing. ETH, CH-6934 Bioggio. E. Grabner, EAWAG, CH-8600 Dübendorf. R. Leoni, Dipl. Ing. ETH, CH-6900 Lugano.

1 M. Gandolla, Gasverwertung bei der verdichteten Deponie Croglio, ISWA Journal *25,* 16 (1978).
2 W. Ryser, Überlegungen zur Gasentsorgung und praktische Hinweise zur Zwangsentgasung, ISWA Journal *25/26,* 25 (1978/79).
3 R. Stegmann, Gase aus geordneten Deponien – Allgemeine Problemstellung, Entstehung und Anfall, ISWA Journal *26/27,* 11 (1978/79).
4 A.J.B. Zehnder, B.A. Huser, Th.D. Brock and K. Wuhrmann, Characterization of an acetate-decarboxylating, non-hydrogen oxidizing methane bacterium, Archs Microbiol. *124,* 1 (1980).
5 Stand der Abfallbeseitung in der Schweiz. Stand Januar 1978. Bundesamt für Umweltschutz, Bern, Switzerland, 1978.
6 G.J. Farquhar and F.A. Rovers, Gasproduction during refuse decomposition, Water, Air and Soil Poll. 2 (1973).
7 K. Winter, Kriterien bei baulichen Einrichtungen auf Deponien hinsichtlich Gefährdung durch Gase. Forschungsbericht 10302102. Erich Schmidt Verlag, Berlin 1979.
8 Sicherheitstechnische Kennzahlen von Flüssigkeiten und Gasen, Schweiz. Unfallversicherungsgesellschaft, eds. Luzern 1976.
9 F. Schuster. G. Leggenwie und I. Skunca, Gas-Verbrennung-Wärme. Essen 1964.
10 P. Hostalier, Die industriellen Gasbrenner. München/Wien 1974.
11 Handbook of Chemistry and Physics, Chemical Rubber Company Publishing.
12 W. Foerst, ed., Ullmanns Enzyklopädie der technischen Chemie, Bd 1, S.333. München 1951.
13 R.H. Collins, Upgrading landfill gas to pipeline specifications, ISWA Journal *28/29,* 1 (1979).
14 J. Nuesch, personal communication.
15 M. Piazzini, communication Turbomach AG.
16 Kabelwerke Brugg, communication.

Future systems

As the previous section indicates, methane cannot easily be stored. Converting it to methanol would reduce its volume and facilitate handling – can this aim be achieved with the help of microorganisms? Knowledge to date on this subject and projects for the future are presented by O. Ghisalba and F. Heinzer.

The final article deals with yet another topic of relevance for the future. Can man mimick photosynthesis in artificial systems? P. Cuendet and M. Grätzel discuss the efforts to overcome the problem of the rather low efficiency in photobiological processes by simplifying the energy storing process as well as the molecular system which transforms light energy into a usable chemical form.

Methanol from methane – a hypothetical microbial conversion compared with the chemical process

by Oreste Ghisalba and Franz Heinzer

Central Research Laboratories of Ciba-Geigy Ltd, CH-4002 Basel (Switzerland)

1. *Introduction*

The synthesis of methanol from organic feedstocks is in effect a conversion of stored solar energy into a liquid fuel. Methanol can be produced chemically via synthesis gas from a variety of feedstocks such as methane (natural gas, associated gas, biogas), biomass (wood, urban and agricultural refuse), coal, heavy fuel oils, shale oils and naphtha (fig. 1). The synthesis gas, a mixture of CO and H_2, is produced from these feedstocks either by steam reforming or by partial oxidation. At present, by far the largest amount of methanol (estimated world production in 1980: 12 million metric tons) is produced from natural gas[1,2]. The conversion efficiency for natural gas in terms of the heating value of methanol as a fraction of the total energy input, which consists of feedstock and processing energy, is about 60% or above[2,3]. In this paper we will consider whether the energy consuming indirect chemical conversion of methane (natural gas) into methanol might be replaced by an energy saving direct microbial oxidation process (fig. 1). The methane used for such a microbial conversion process could either be natural gas or biogas obtained by anaerobic digestion of biomass. To assess the feasibility of a microbial conversion we must first have a closer look at the well-known petrochemical conversion process.

2. *The chemical methanol synthesis based on methane*

The technical methanol synthesis based on methane is characterized by the 3 equations below[1,4,5]:

(1) steam reforming

$$CH_4+H_2O \xrightarrow[\substack{700\text{-}900\,^\circ C\\ 1\text{-}25\text{ bar}}]{\substack{\text{Ni-catalyst}\\ (15\text{-}20\%\text{ on }Al_2O_3\text{ or }SiO_2)}} CO+3\,H_2,$$

$$\Delta H_{800}=+226.9\text{ kJ/mole}$$

(2) shift reaction

$$CO_2+H_2 \xrightarrow{\text{Ni-catalyst}} CO+H_2O, \qquad \Delta H_{25}=+38.5\text{ kJ/mole}$$

(3) low pressure methanol synthesis

$$CO+2\,H_2 \xrightarrow[\substack{230\text{-}280\,^\circ C\\ 50\text{-}100\text{ bar}}]{\text{Cu-catalyst}} CH_3OH, \qquad \Delta H_{25}=-90.9\text{ kJ/mole}$$

The steam reforming of methane in this highly endothermic reaction (1) yields a synthesis gas too rich in hydrogen for the methanol synthesis (3). By adding 33% of CO_2 the CO/H_2 ratio can be shifted to the ideal value of 1:2 (2). If no CO_2 is available, excess hydrogen is purged from the methanol synthesis loop and burned as a fuel which can be used for the process[6]. Methanol is finally synthesized according to the exothermic step (3) from synthesis gas. The reactors constructed today follow exclusively the energy saving 'low pressure' concept (ICI, Lurgi, MGC process) at 230–280 °C and 50–100 bar[6,7]. The highly active catalysts used for this process are copper-based (together with metals like Zn, Al, Cr, Mn, V) and thus very sensitive to sulfur compounds. The sulfur content in the synthesis gas has to be below 0.1 ppm! The life-expectation of these catalysts is 3–4 years.

Low temperatures and ultra pure catalysts reduce the formation of unwanted by-products such as methane, dimethylether, higher alcohols and hydrocarbons to about 1%. Highly pure methanol (99.99%) is finally obtained by 2 successive distillations[6]. The table illus-

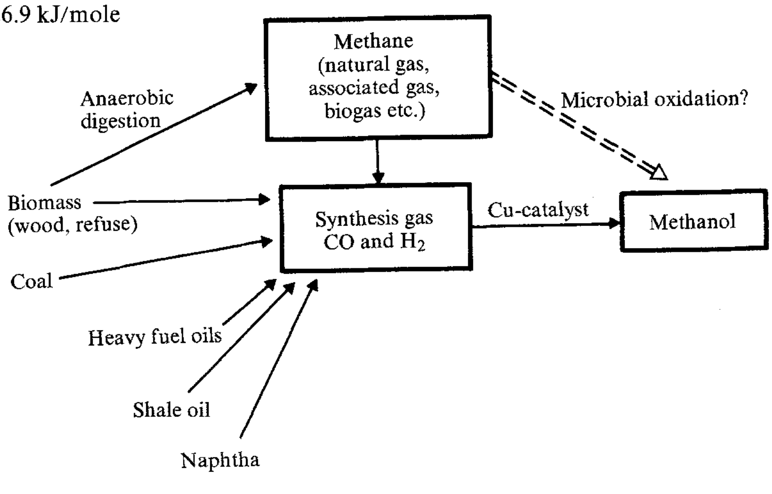


Figure 1. Methanol synthesis from various feedstocks.

Typical requirements per metric ton of methanol produced from methane by low pressure processes[7]

	ICI**	MGC**	Lurgi*
Feed and fuel (natural gas, GJ)	31.0	32.7	29.3
Electric power (kWh)	35	20	50
Feed water (m^3)	1.15	1.2	0.76
Cooling water (m^3)	70	100	45
Catalyst cost (US-dollars)	0.9	no data	1.02
Capacity of operating plants (tons/day)	50-1800	10-600	130-1360
Capacity of plants under construction (tons/day)		2000-4000	450-2000

ICI, Imperial Chemical Industries Ltd.; MGC, Mitsubishi Gas Chemical Co., Inc., * CO_2 available; ** no CO_2 available.

trates the energy and feed requirements for 3 typical modern low pressure processes.

3. *Wood as a feedstock for methanol synthesis*

Wood is a very interesting base for methanol production because it represents stored solar energy in the form of partially reduced carbon compounds and unlike petrochemical sources it is a renewable chemical feedstock. The interest in the economic feasibility of methanol production based on wood as a feedstock is worldwide[2,5]. So far there are no methanol plants operating on an industrial scale which use wood as a feedstock. Results from pilot plant studies in the United States and Canada[5] suggest that it is technically feasible but not as yet economically attractive to produce methanol from wood. Compared with natural gas (conversion efficiency above 60%) the energy yields for methanol from wood are poor. For a wood waste plant, the conversion efficiency is only 38% (heating value of methanol as a fraction of the total energy input into the plant)[5]. In addition the calculated investment costs for an industrial wood-based methanol plant (200,000 tons per year) are about 3 times higher than for a conventional natural gas facility[5]. However, in areas with large wood resources and high transport costs for petrochemical feedstocks (natural gas, petroleum) the production of methanol (via synthesis gas) from wood or refuse might become economically and ecologically attractive in the near future.

4. *Utilization and properties of methane and methanol*

Methane and methanol are important basic chemicals for the petrochemical industry and for the generation of energy (see fig. 2).

Sources of methane (world resources 70-230 · 10^{12} m^3)[8]: Natural gas[9] containing 65-95% methane, 1-6% ethane and 0-25% N_2, CO_2 H_2S, associated gas[9] containing 50-85% methane, 8-20% ethane, 3-12% propane and 0-10% CO_2 and biogas[10] containing 70% methane, 29% CO_2 and 1% H_2.

Storage and transport of methane: Methane can be liquified and stored at −162 °C under atmospheric pressure (estimated world production 1980: 43 · 10^9 m^3 liquified natural gas (LNG)[8]). Natural gas is transported either by pipelines or as LNG by refrig-

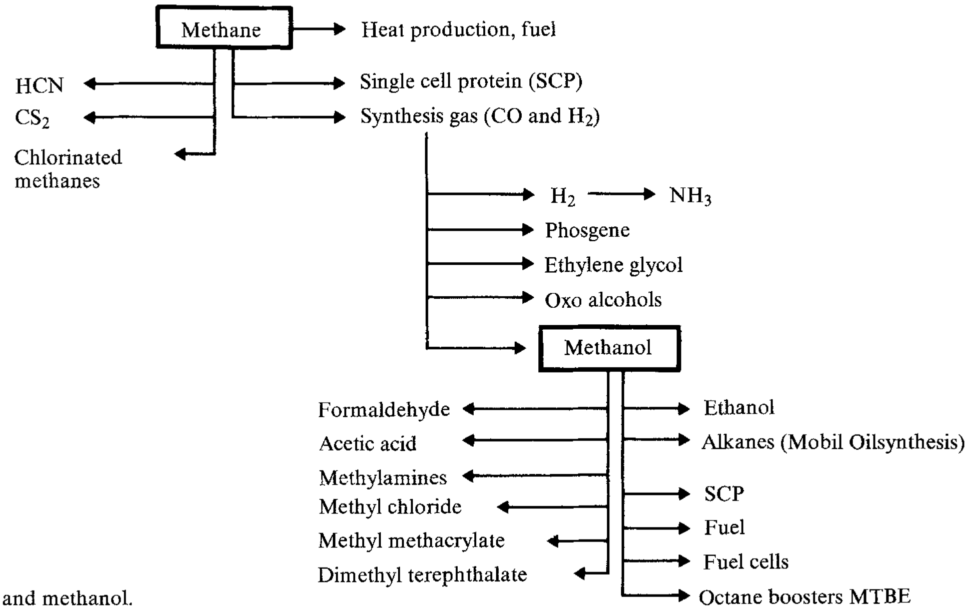


Figure 2. Utilization of methane and methanol.

erated tankers. LNG is condensed to $\frac{1}{600}$ of the original volume of natural gas and is thus easier to store in large amounts. However, storage and transport of natural gas or LNG are both expensive and hazardous[8,11].

For political and commercial reasons (including the transport and storage problems mentioned above) large amounts of associated gas from production fields are still flared. For Saudi Arabia the reported amount of flared associated gas is $40 \cdot 10^9$ m^3 per year[8] and for all the OPEC states together a figure of 60% is given[12]. These annual losses in the Near East alone are equal to about 16% of the United States annual gas consumption[2]. This waste of a non-renewable resource should be stopped or at least reduced in the near future. Instead of undergoing the expensive and hazardous transport in pipelines or LNG-tankers, natural gas or associated gas could be converted into methanol and other derivatives on the spot. Methanol can be transported or stored as easily as gasoline and would be much cheaper and less risky to handle than natural gas or LNG. It is predictable that methanol will have a more important role as a basic petrochemical building block and as a source for energy generation in the future because of the multisources of synthesis gas[9]. Methanol is among the 20 most important organic chemicals[13]. The world production for 1980 is estimated to be 12 million tons but extrapolations predict a production of 68 million tons (or even more optimistic 200 million tons) of methanol for 1985[9]. Predicted uses for 1985 are: peak power generation (42%), established chemicals (25%), gasoline (21%), steel fabrication (6%), single cell protein (4%) and sewage treatment (2%)[9].

5. *Bioconversion or petrochemical synthesis?*

At present no *direct* chemical conversion of methane into methanol using less drastic conditions than those already described is known. All the processes in operation today synthesize methanol indirectly via synthesis gas. Studies on the direct catalytic oxidation of methane by a one-step reaction report only poor yields.

In contrast to ethanol, which can be produced from organic substrates such as sugars or cellulose by fermentation processes with yeasts or bacteria, no direct fermentation process for the production of methanol is known so far. The microbial production of methanol from organic substrates might involve the following steps (see also fig. 1):

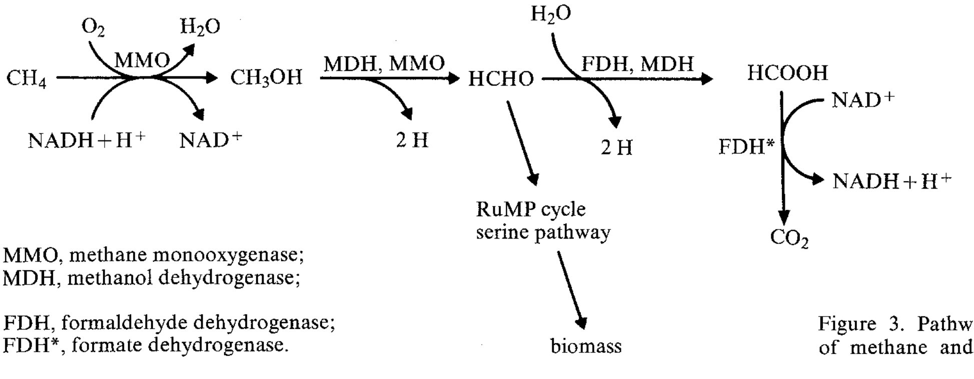
1. Anaerobic digestion of biomass (manure, wood waste etc.) to produce biomethane (biogas). The theoretical fuel energy conversion efficiency for this process is reported to be above 90%[3].
2. Bioconversion of methane (natural gas, biogas) into methanol. The conversion efficiency of this step should be comparable or even better than the efficiency (above 60%) reached in the low pressure synthesis based on natural gas (theoretical maximum about 80%).

A semi-biological process could also be envisaged: low pressure methanol from biogas (step 1 followed by the chemical methanol synthesis described in section 2).

A considerable number of microorganisms (bacteria and yeasts), the methanotrophs or methylotrophs, are known to be able to grow on methane and/or methanol (and sometimes also on various other C_1 compounds such as methylamines, formamide, formate etc.) as the sole source of carbon and energy. Some years ago, Foo and Heden[3,14] proposed the use of such organisms for the biocatalytic production of methanol starting from methane. Since that proposition (1977/78) no practical results have been reported. Nevertheless, the idea is still very attractive. During the last few years a great deal of information on the physiology of the methylotrophs and especially on the mechanisms and enzymes of methane oxidation has been published.

6. *Methanotrophy – physiology of methane oxidation*

The microorganisms utilizing C_1 compounds are divided into 2 major groups, the obligate methylotrophs (growth only on C_1 compounds such as methane, methanol, methylamines etc.) and the facultative methylotrophs (growth on C_1 compounds or



MMO, methane monooxygenase;
MDH, methanol dehydrogenase;

FDH, formaldehyde dehydrogenase;
FDH*, formate dehydrogenase.

Figure 3. Pathway for the bacterial oxidation of methane and methanol.

other organic substrates such as acids, sugars etc.). In the following discussion we will concentrate on the methane-utilizing isolates (methanotrophs).

The obligate methanotrophs are generally classified into 5 genera: *Methylococcus, Methylomonas, Methylobacter, Methhylosinus* and *Methylocystis*[14-21]. All these organisms possess a complex internal arrangement of paired membranes either as bundles of vesicular discs (type I, in *Methylococcus, Methylomonas, Methylobacter*) or as layers around the periphery of the cells (type II, in *Methylosinus, Methylocystis*). These membranes are most probably involved in methane oxidation[18,20]. Only few facultative methanotrophs have been studied and described e.g. *Methylobacterium organophilum*[22] and *Methylobacterium* R6[23].

The pathway of methane oxidation used by the methanotrophs is shown in figure 3 (for details see the reviews 14-21, pool of data from different organisms). The oxidation of methane to CO_2 is thought to proceed via a series of two-electron oxidation steps. Each step is sufficiently exergonic to permit, at least theoretically, the generation of 1 or more equivalents of ATP, but this has yet to be demonstrated. Formaldehyde occupies a central position in the oxidation of methane, for it is the branch point intermediate from where carbon is both assimilated into biomass (70%) via the ribulose monophosphate pathway (type I-organisms) or the serine pathway (type II-organisms) and dissimilated to CO_2 (30%) to provide energy for growth. The methane monooxygenase reaction (MMO) in *Methylococcus capsulatus, Methylomonas methanica (Pseudomonas methanica)* and *Methylosinus trichosporium* requires NADH as a cofactor (electron donor) whereas the cofactor for methanol dehydrogenase reaction (MDH) seems to be PQQ[28]. The formaldehyde dehydrogenase reaction (FDH) is mediated by different isoenzymes which are either dependent on NAD and glutathione *(Methylomonas methanica)* or NAD-independent. In *Methylococcus capsulatus* methanol oxidation and formaldehyde oxidation are both catalyzed by one single bifunctional methanol dehydrogenase. The formate dehydrogenase reaction (FDH*) is NAD-dependent in *Methylococcus capsulatus, Methylomonas methanica* and *Methylosinus trichosporium.*

For a biocatalytic production of methanol, MMO and MDH are the 2 relevant target enzymes at which we should have a closer look.

7. *Methane monooxygenase (MMO)*

Methane monooxygenase has been intensively studied in 3 methanotrophs: *Methylomonas methanica, Methylococcus capsulatus* and *Methylosinus trichosporium*[14-21]. The oxygen in the resulting methanol was shown to be exclusively derived from dioxygen. All the investigated MMOs involve cytochromes and show specific requirement for NADH as the electron donor. Ethane was also oxidized by the enzyme preparations.

The enzyme of *Methylococcus capsulatus* oxygenates a quite extraordinary range of compounds in addition to methane (co-oxidation) e.g. methanol, methane derivatives, n-alkanes, n-alkenes, ethers, alicyclic, aromatic and heterocyclic compounds. The enzyme thus shows a rare lack of substrate specificity[20]. The MMO of *Methylomonas methanica (Pseudomonas methanica)* was found to oxygenate the substrate analog bromomethane as well as ammonium chloride. The enzyme was inhibited by dithiothreitol, reduced glutathione and cyanide[20]. The MMO of *Methylosinus trichosporium* is possibly not obligatorily NAD-dependent. Ascorbate and methanol, in the presence of low concentrations of phosphate, were also effective electron donors[20]. However, these findings could not be reproduced by other researchers[19] and NADH is said to be the only effective electron donor. The MMO of *Methylosinus trichosporium* has a substrate specificity quite similar to that of *Methylococcus capsulatus* but the system of *Methylomonas methanica* is more restricted[19].

8. *Methanol dehydrogenase (MDH)*

In cell suspensions of *Methanomonas methanooxidans* (Brown and Strawinski) it was reported that 3 mM iodoacetate inhibited methanol oxidation but not methane oxidation and 75% of the consumed methane were accumulated as methanol[3,24]. However, these findings could not be reproduced by other researchers[25]. In fact it has been found that iodoacetate inhibits methane oxidation more than methanol oxidation[20,26]. Small amounts of methanol can be obtained from cell suspensions of *Methylomonas methanica* or *Methanomonas methanooxidans* at phosphate concentrations of 70-80 mM[3,26]. In cell free extracts of *Methylosinus trichosporium* the MDH activity was inhibited with 150 mM phosphate buffer[20,27] and also EDTA was found to have an inhibitory effect in the same system[3,14].

The MDHs of *Methylomonas methanica, Methylosinus trichosporium, Methylosinus sporium* and *Methylococcus capsulatus* can be coupled via phenazine methosulfate to oxygen or to artificial electron acceptors such as 2,6-dichlorophenol indophenol or cytochrome c[19,20]. Ammonia or methylamine act as activators and the enzyme has a broad substrate specificity, being able to oxidize primary alcohols and formaldehyde. For some methanol- but not methane-utilizing methylotrophs the cofactor of MDH has recently been identified as a new coenzyme PQQ[28].

9. *Research program for biocatalytic methane oxidation*

The following basic steps must be taken to establish a bioconversion process as proposed in section 5.

- Selection of highly efficient obligate and/or facultative methanotrophs including genetic improvement of strains (criteria: high MMO activity, reasonable generation time, increased methanol tolerance, eventually application of thermophilic strains).
- Studies on the regulation of methane and methanol oxidation. Activation of MMO and inhibition of MDH. Search for selective inhibitors of MDH which should not affect the methane oxidation.
- Search for artificial electron donors in vivo and in vitro to replace NADH in the methane monooxygenase reaction (eventually application of electroenzymological methods or co-oxidation systems). The energy metabolism is one of the crucial problems in this program.
- Selection of methanol accumulating mutants. Several types of mutants are possible: MDH$^-$-mutants (facultative methanotrophs) or cytochrome c mutants. Cytochrome c is involved in electron transport during the methanol oxidation reaction.
- Studies on immobilization and stability of MMO or intact cells.
- Construction of a methanol producing bioreactor using immobilized cells or enzyme systems.

With our present knowledge it cannot yet be decided whether an obligate or a facultative methanotroph is more suitable for this work or whether the inhibition of the methanol oxidation is easier to achieve with inhibitors or by mutation. The knowledge acquired from the production of single cell proteins with methane and methanotrophs will be very helpful for the plant design.

10. *Outlook*

The major advantage of a biotechnological process for the conversion of methane into methanol compared with the petrochemical synthesis are the mild transformation conditions. Atmospheric pressure and low temperatures (maximum 60 °C for thermophilic strains) would be sufficient for a microbial process. Thus one would expect remarkable process energy savings, even in comparison with the modern low pressure chemical methanol synthesis. In addition the investment costs for a large scale methanol fermentation plant should be rather lower than for a conventional synthesis gas methanol plant. So far our comparison has dealt with large industrial facilities. But we should not forget that a microbial process has one major advantage over a petrochemical process, namely, microbial processes are the only choice for decentralized small and medium sized facilities. Even if a microbial conversion process might not be economically feasible on a large scale its ecological and economical advantages are obvious in the field of small technology. On the other hand a petrochemical methanol synthesis is not considered to be of economical interest on a scale below about 10,000 tons a year. A very attractive combination of 2 biological processes feasible on a small scale (for farms, villages etc.) would be methane production by anaerobic digestion of biomass followed by bioconversion into methanol. Thus storage and transportation problems associated with methane (biogas etc.) might be overcome. Such a combined biotechnological process allows the decentralized production of a liquid fuel based on renewable biomass.

* Acknowledgment. The authors thank J.A.L. Auden, J. Konecny, M. Küenzi and J. Nüesch for reviewing this manuscript.

1 F. Marschner, F.W. Möller and H.P. Gelbke: Methanol, in: Ullmanns Enzyklopädie der technischen Chemie, 4th edn, 1978, vol. 16, p. 621.
2 N.P. Cheremisinoff: Gasohol for Energy Production. Ann. Arbor Science Publ., Ann. Arbor, Mich., 1979.
3 E.L. Foo and G.C. Hedén, Is a biocatalytic production of methanol a practical proposition?, in: Microbial Energy Conversion, p. 267. Ed. H.G. Schlegel and J. Barnea. Pergamon Press, New York 1977.
4 H. Pichler and A. Hector, Synthesegas, in: Ullmanns Enzyklopädie der technischen Chemie, 3rd edn 1965, vol. 16, p. 599.
5 R.M. Rowell and A.E. Hokanson, Methanol from wood: A critical assessment, in: Progress in Biomass Conversion, vol. 1, p. 117. Ed. K.V. Sarkanen and D.A. Tillman. Academic Press, New York 1979.
6 J.A. Camps and D.M. Turnbull, Synthetic Gas production for Methanol: Current and Future Trends, in: Hydrogen: Production and Marketing, p. 123. Ed. W.N. Smith and J.G. Santangelo. ACS Symposium Series 116, American Chemical Society, Washington, DC, 1980.
7 Petrochemical Handbook 1979 Issue, Hydrocarb. Process., November 1979, p. 115.
8 Anon., Die grosse Zeit der Gasmänner. Der Spiegel Nr. 42, p. 79 (1979).
9 L.F. Hatch and S. Matar, From Hydrocarbons to petrochemicals, part 6 Petrochemicals from methane. Hydrocarb. Process., October 1977, p. 153.
10 J. Lawrie: Natural Gas and Methane Sources. Chapman and Hall, London 1961.
11 L.N. Davis: Gambling on 'frozen fire'. New Scient. *85,* 70 (1980).
12 L.F. Hatch and S. Matar, From Hydrocarbons to petrochemicals, part 1-Natural and associated gas. Hydrocarb. Process., May 1977, p. 191.
13 H.H. King, R. Williams and C.A. Stokes, Methanol - Fuel or Chemical? Hydrocarb. Process., June 1978, p. 141.
14 E.L. Foo, Microbial Production of Methanol. Process Biochem. *13,* 23 (1978).
15 D.W. Ribbons, J.E. Harrison and A.M. Wadzinski, Metabolism of single carbon compounds. A. Rev. Microbiol. *24,* 135 (1970).
16 J.R. Quayle, The Metabolism of One-Carbon Compounds by Micro-Organisms. Adv. Microbiol. Physiol. *7,* 119 (1972).
17 N. Kosaric and J.E. Zajic: Microbial Oxidation of Methane and Methanol. Adv. Biochem. Engng *3,* 89 (1974).
18 C. Anthony, The biochemistry of methylotrophic micro-organisms. Sci. Prog., Oxford *62,* 167 (1975).
19 J. Colby, H. Dalton and R. Whittenbury, Biological and biochemical aspects on microbial growth on C_1 compounds. A. Rev. Microbiol. *33,* 481 (1979).
20 R.S. Wolfe and I.J. Higgins, Microbial Biochemistry of Methane - A Study in Contrasts. Int. Rev. Biochem., Microbiol. Biochem. *21,* 267 (1979).
21 R. Whittenbury, K.C. Phillips and J.F. Wilkinson, Enrichment, Isolation and Some Properties of Methane-utilizing Bacteria. J. gen. Microbiol. *61,* 205 (1970).
22 T.E. Patt, G.C. Cole and R.S. Hanson, Methylobacterium, a New Genus of Facultatively Methylotrophic Bacteria. Int. J. Syst. Bact. *26,* 226 (1976).

23 R.N. Patel, C.T. Hou and A. Felix, Microbial Oxidation of Methane and Methanol: Isolation of Methane-utilizing Bacteria and Characterization of a Facultative Methane-Utilizing Isolate. J. Bact. *136*, 352 (1978).
24 L.R. Brown, R.J. Strawinski and C.S. McCleskey, The Isolation and Characterization of *Methanomonas methanooxidans* Brown and Strawinski. Can. J. Microbiol. *10*, 791 (1964).
25 J.F. Wilkinson, Physiological Studies of Bacteria Grown on Methane, in: Microbial Growth on C_1 Compounds, p.45. Ed. The Society of Fermentation Technology, Japan 1975.
26 I.J. Higgins and J.R. Quayle, Oxygenation of Methane by Methane-Grown *Pseudomonas methanica* and *Methanomonas methanooxidans*. Biochem. J. *118*, 201 (1970).
27 G.M. Tonge, D.E.F. Harrison, C.J. Knowles and I.J. Higgins, Properties and partial purification of the methane-oxidizing enzyme system from *Methylosinus trichosporium*. FEBS Lett. *58*, 293 (1975).
28 J.A. Duine, J. Frank and P.E.J. Verwiel, Structure and Activity of the Prosthetic Group of Methanol Dehydrogenase. Eur. J. Biochem. *108*, 187 (1980).

Artificial photosynthetic systems

by Pierre Cuendet and Michael Grätzel*

Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne (Switzerland)

Presently endeavors are being undertaken to design systems capable of converting solar radiation into fuels. These efforts are timely and mandatory in order to reduce our dependence on fossil energy reserves. Recently there has been an explosion of information on this subject[1–13] and a multitude of processes are under investigation which attempt to mimic photosynthesis. The present article gives a brief overview over these artificial systems and explains some basic principles of their operation.

Plant photosynthesis serves to convert light into energy-rich compounds such as carbohydrates. This biological device is, however, a rather poor energy converter if the amount of biomass produced by the incident solar flux is considered. Although the primary photoredox reactions that occur in the chloroplasts proceed with high quantum efficiency the overall conversion yield is approximately 5-6% and falls to 1-3% at best when averaged over the whole year[14]. Major losses are due to growth, adaptation and reproduction processes. Thus the photosynthetic machinery could work more efficiently had it been designed mainly for fuel production without any constraints due to evolutionary history[15].

Artificial systems try to overcome this shortcoming of the biological counterpart by simplifying both the energy storing process and the molecular units that accomplish this transformation. Three different approaches are presently being pursued. In the first or hybrid system the thylakoid membranes or individual photosystems are employed as light harvesting units. The objective is to exploit the high efficiency of the primary photosynthetic redox events without attempting to synthesize carbohydrates from CO_2. Instead, hydrogen generation from water is achieved through artificial redox relays and catalysts.

The second approach is to employ synthetic molecular assemblies such as micelles or membranes as reaction systems. These aggregates simulate the microenvironment present in biological systems and serve as a host for hydrophobic entities participating in the photoreactions.

Finally, artificial systems with very little resemblance to their biological counterpart are also under study. Prominent and promising at the same time are here colloidal semiconductor solutions.

None of the presently available model systems will achieve the conversion of carbon dioxide into sugar under illumination with visible light. However, they will perform other more simple endoergic transformations such as the photocleavage of water and the production of methanol from CO_2.

Hybrid systems

Before the recent development of bifunctional catalysts and the design of totally artificial systems, which will be described later, the photolysis of water by visible light was achieved only by the chloroplast and cyanobacteria machinery. The light-induced water decomposition

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2} O_2 \qquad (1)$$

is an attractive means by which to convert solar photon energy into chemical potential. Cell-free hybrid systems, composed of isolated chloroplasts coupled to suitable redox catalysts have been shown to achieve this decomposition[16]. Figure 1 illustrates

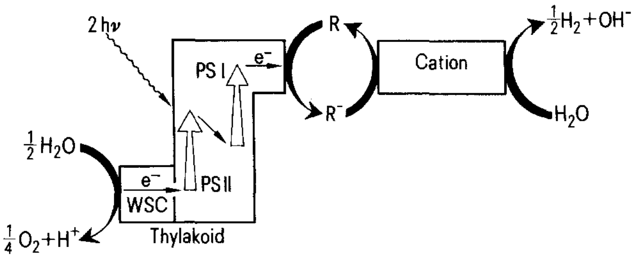


Figure 1. Schematic illustration of a cell-free hybrid system for the biophotolysis of water.