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Alternative resources for the methanol economy

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Abstract. Generally, methanol produced for chemical applications is made predominantly *via* fossil resources. But it can also be obtained from any carbon-containing feedstock, including biomass, biogas, forest residues, and municipal or other waste products. Perspective viewing and critical assessment show the possibilities and constraints of such alternative resources for the realization of the methanol economy with high sustainability. The bibliography includes 57 references.

I. Introduction

Back in the mid-1980s, Friedrich Asinger prophesied in his book 'Methanol — a Chemistry and Energy Raw Material' that 'Become once the fossil raw material resources even more limited and more expensive or these go completely to an end [...] remains except the biomass only [...] carbonic acid as a raw material resource' (Ref. 1, pp. 20 – 22), which with the low-cost hydrogen from alternative resources will be a basic material for methanol synthesis. Methanol is a very convenient key substance because after the MTO (methanol to olefins), MTG (methanol to gasoline) and MTA (methanol to aromatics) processes by zeolite catalysis, practically the whole palette of petrochemistry products can be obtained from methanol. Thus, the contemporary chemistry has a unique chance to bring in its comprehensive knowledge and take part in the creation of the prospective bio-based product family tree.[2, 3]

For this reason, George A Olah, the Nobel Prize Laureate in chemistry of 1994, has proposed the so-called 'methanol economy' as a reasonable alternative. He wrote: 'Methanol provides an efficient means to store energy and can be used as a convenient fuel as well as a raw material for manmade hydrocarbons and their products'.[4]

One of the most remarkable aspects of methanol is the diversity of feedstocks which can be used for its production, whereby methanol can be obtained from any resource that can be converted first into synthesis gas. The basic raw materials used for the supply of synthesis gas changed more than once since the industrial production of methanol started. In the beginning, coal was practically the only feedstock, whereas today, natural gas has mostly replaced it. During a period roughly comprising the 1960s and 1970s, crude oil fractions, such as light naphtha or residual oil, were the preferred feedstocks. The costs were decisive for the choice of the raw material. With respect to cost, it must be pointed out that the costs for synthesis gas production account for a large part of the investment costs for a methanol plant (Ref. 5, p. 807).

In the future, a great and increasing amount of methanol will be produced from renewable and sustainable resources. This includes every kind of biomass, biogas, agricultural and timber waste, solid municipal waste, and other feedstocks.

In principle, methanol can be obtained from biomass in two different ways. 'Dry' biomass (*e.g.* waste wood) can be gasified, generating a gas mixture that has to be conditioned in order to obtain a parent gas which is suitable for methanol synthesis.[6] A biogas which is rich in methane can be produced from 'wet' biomass (*e.g.*, biodegradable waste) by means of fermentation. This biogas then has to be subjected to several stages of gas treatment as well.[7] Pathways for the production of methanol from biomass resources, including the respective stages of synthesis gas and biogas preparation, are illustrated in Fig. 1.

The gasification of 'dry' biomass produces a gas mixture composed mainly of CO, CO_2, H_2, H_2O, CH_4 and higher hydrocarbons as well as condensable aromatic compounds (tar). Such tar can condense at a temperature below 300 – 400 °C and cause severe damage in the downstream processes. Furthermore, the obtained gas contains small amounts of contaminants such as dust, sulfur compounds,

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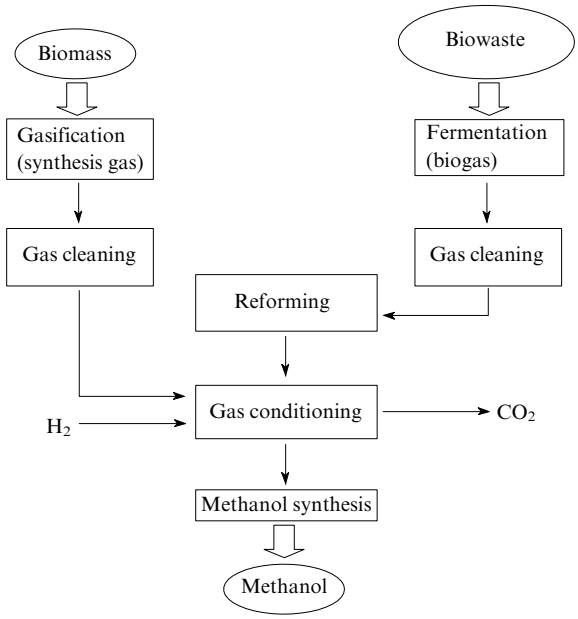
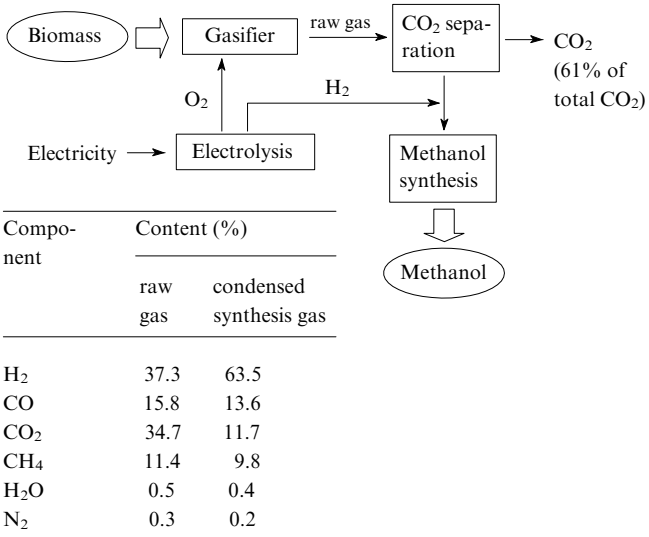


Figure 1. Simplified schematic illustrating methanol production from biomass-based feedstocks.



Component	Content (%)	
	raw gas	condensed synthesis gas
H_2	37.3	63.5
CO	15.8	13.6
CO_2	34.7	11.7
CH_4	11.4	9.8
H_2O	0.5	0.4
N_2	0.3	0.2

Figure 2. Flow diagram for methanol synthesis from biomass including hydrogen generation by electrolysis. Since there is still a hydrogen deficit, carbon dioxide has to be removed from the raw gas.[8]

ammonia, halogens, *etc*., some of them are catalyst poisons and adversely affect downstream synthesis processes. Therefore, a requirement profile was defined for the biomass gasification process as the preliminary stage in methanol production. These requirements include a mostly inert gas-free raw gas with a high rate of hydrogen and the lowest possible content of dust and tar.

The methanol synthesis reactions are described by the following equations (Scheme 1).

Scheme 1

$$CO + 2\,H_2 \rightleftharpoons CH_3OH, \qquad \Delta_R H = -92 \text{ kJ mol}^{-1}$$

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O, \quad \Delta_R H = -50 \text{ kJ mol}^{-1}$$

The stoichiometry factor of the synthesis gas mixture

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

has to be at least $S = 2$ in order to observe a high methanol yield. Due to the stoichiometric composition, biomass gasification always produces a parent gas with an H_2 content that is too low and a CO_2 content that is too high for methanol synthesis. If the requirement $H_2/CO > 2$ is not fulfilled, the synthesis gas has to be conditioned in stoichiometric terms by separating CO_2 from the produced raw gas and/or by adding hydrogen by means of (regenerative) electrolysis. The correlation between the rates of CO, CO_2 and hydrogen in the biomass-based synthesis gas and the methanol yield and selectivity that can be achieved with it was examined and described in detail by Yin *et al*.[8] A flow diagram of this process and the corresponding synthesis gas composition are represented in Fig. 2.

With this procedure, a biomass input of 2 t h^{-1} (waste wood) requires ~5 MW of electric power and produces about 1.2 t h^{-1} of methanol.[9] However, the necessary separation of a large part of the CO_2 (more than 60%) reduces the conversion of the biomass carbon into methanol to ~45%.

The production of methanol on the basis of biogas consisting mainly of methane and carbon dioxide together with some undesired components requires a complex gas cleaning process and also an additional heterogeneous catalyzed reforming step followed by another gas conditioning process. The catalytic reforming process of methane takes place at the same time as the water gas reaction, in which carbon monoxide and water vapour are converted into carbon dioxide and hydrogen. Carbon dioxide can then further react with hydrogen and form methane (Sabatier reaction) (Scheme 2):

Scheme 2

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2, \qquad \Delta_R H = 206 \text{ kJ mol}^{-1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \qquad \Delta_R H = -41 \text{ kJ mol}^{-1}$$

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O, \quad \Delta_R H = -253 \text{ kJ mol}^{-1}$$

When reformed biogas is used, the carbon dioxide content in the synthesis gas is much higher, resulting in a stoichiometry factor which is significantly less than 2. By means of pressure swing adsorption (PSA), the H_2/CO ratio that is ideal for methanol synthesis is achieved by separating carbon dioxide from the raw gas. It has to be noted that in this case, too, satisfactory conversion of the biomass carbon can only be achieved by introducing hydrogen (produced in a regenerative way). The synthesis gas produced in this way is purified, compressed, and converted into methanol by means of heterogeneous catalysts. Without any additional electrolytic hydrogen supply, and with a carbon dioxide separation of 95%, the carbon conversion drops to about 20% with a methanol production of only 0.6 t h^{-1} based on a wood input of 2 t h^{-1} as a feedstock.[10] According to other reports, this procedure can produce two tonnes of methanol

(96% pure) from 1 500 m^3 of biogas generated from 100 tonnes of liquid sludge per day.[11]

As the basis of the feedstock changed with the time, the typical site and size of methanol plants changed accordingly. While methanol plants used to be 'world scale' facilities situated in industrial centres within chemical production complexes where methanol was required or processed, new plants built in the past few years are always 'stand alone' facilities, often with lower capacities. In the new plants, the generation of synthesis gas or biogas as the preliminary stage of methanol production is based mainly on the utilization of organic residues. Seeing this, the production of methanol based on biological resources seems very promising at the moment, particularly because the individual process steps are for the most part known, and sound cost-benefit calculations for large industrial plants are available as well (see Ref. 5, p. 808).

II. Wood

Of all the types of biomass, wood has the best properties for utilization as raw material for the chemical industry and for power generation (see Ref. 1, pp. 17–19). However, in some regions this is overrated, particularly at a time in which certain countries are suffering from catastrophic wood shortages. Therefore, this raw material is given priority here.

For 2005, the total volume of the accumulated wood from all forests in the entire world was estimated at 422 gigatonnes by the FAO (Food and Agriculture Organization of the United Nations).[12] The distribution of the world's forests is illustrated in Fig. 3. Every year, 3.2 billion m^3 of raw wood are cut, almost half of it in countries in the tropics. But with 2.3 m^3 ha^{-1}, Western Europe presents the highest annual cutting rate. However, power generation still remains the most important type of wood utilization. Almost 50% of the global timber is used as firewood, particularly in countries in the tropics. In Western Europe, firewood only accounts for almost a fifth of the wood cut. In 2009, wood accounted for approximately 3% of the total primary energy supply which, taking the lack of subsidies into account, must be seen as an economic success.[13]

Wood is considered a renewable source of raw material and energy, provided that the volume used does not exceed the volume regrown. The fact that it is simple to process and accordingly requires little energy for production and processing is another important factor in its ecologic assessment. In specific regions of the world that have at their disposal only small oil and gas resources, if any, wood can play a decisive role as a raw material for the chemical industry and for power generation if the organizational and logistical prerequisites — with respect to the collection of waste wood, transportation, infrastructure, *etc.* — are fulfilled. The differences among individual types of wood and the diversity of their respective usage constitute additional problems which have to be considered.

The plant cell walls typically consist of cellulose (40 mass % – 50 mass %) hemicellulose (25 mass % – 40 mass %), lignin (20 mass % – 30 mass %), and small amounts of so-called extractives (2 mass % – 10 mass %), as well as a number of inorganic compounds (0.2 mass % – 0.8 mass %) representing the major source of ashes when the biomass is combusted.[14] Fresh biomass contains up to 60% – 70% water and must be dehumidified prior to gasification to reduce the water content to 15%. In order to constitute an economically attractive feedstock, it should cost only half as much as coal, calculated on the basis of the same heating value. Table 1 indicates the composition and heating values of hard and brown coal as well as peat and wood on a dry, ash-free basis.

However, coal mining and oil production hardly take up any surface area, while the production of all kinds of biomass requires large areas and a suitable climate. Therefore, from an economic point of view, such raw materials

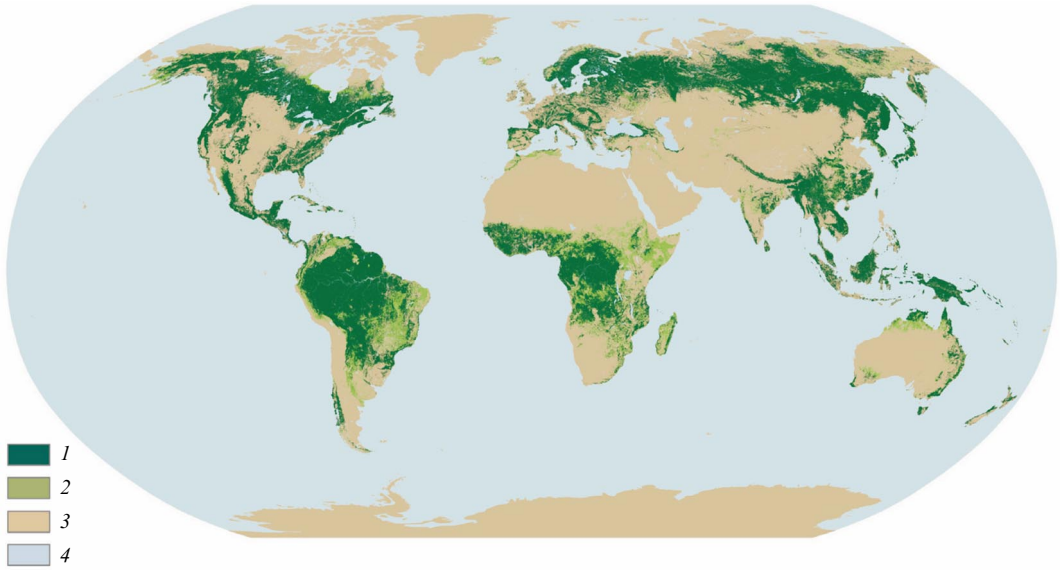


Figure 3. Distribution of the world's forests, recorded by FAO.[12]
(*1*) Forest, (*2*) other wooded land, (*3*) other land, (*4*) water.

Table 1. Comparison of the composition of completely dry hard coal, brown coal, peat and wood on an ash-free basis (see Ref. 1, p.19).

Feedstock	Elemental compostion (%)					Heating value /kJ kg^{-1}	
	C	H	O	N	S	minimum	maximum
Hard coal	79.5	4.7	12.7	1.4	1.7	31 100	32 100
Brown coal	66.6	4.9	26.9	1.2	0.4	25 500	26 600
Peat	56.9	5.7	35.9	1.3	0.2	21 800	23 000
Wood	49.5	6.1	44.1	0.3	0.02	18 400	19 700

are of interest only for countries with a very large surface area but little oil, gas and coal resources.

In the long run, wood-based methanol production is the most cost-efficient method of producing energy carriers according to specifications based on regenerative raw materials. It is superior to every other process in terms of the total calorific efficiency, the expense for cultivation and harvesting, and the net yield per hectare. Wood is planted every 10 to 30 years, can be harvested and used throughout the entire year, and does not cause any environmental problems. Wood ash from the gasification process is conveniently returned to the soil. This is possible due to its high melting point; it does not form slag. The melting point is important for the gasification process, because the gasification temperature can be as high as 1100 °C, increasing the specific throughput in the gasifier due to the higher gas velocity of oxygen and water vapour.

In the course of the discussions about the increasing utilization of regenerative raw materials at the beginning of the 21st century, wood gasification and gasification of organic residues for the purpose of producing synthesis gas or gaseous fuels for heat and power generation became the subject of a growing number of research projects, and were put into practice in individual demonstration plants. Wood from forests as well as agricultural lignocellulosic biomass is particularly suitable as feedstock. Lignocellulosic biomass primarily includes stalk material such as crop and corn straw as well as other residues from the agricultural cultivation of crops. This is complemented by energy crops such as *Miscanthus giganteus* as well as poplar and willow wood cultivated on short rotation plantations.[15] Compared to biomass containing starch or sugar, such as wheat, corn, sugar beets and sugar cane, *etc*., the net yield of wood-based methanol is 1.5–2 times as high, based on the same heating value.

Although wood, compared to coal, contains little nitrogen, sulfur and ash (see Table 1), it is not an ideal feedstock for gasifiers. Some of the inherent problems like low bulk density, high moisture content, hydrophilic nature, and low heating value render raw biomass difficult to use in a large scale gasifier. Moreover, for feedstocks with low O/C ratios, such as coal, higher gasification efficiencies than for wood with high O/C ratios can be observed.[16] Therefore, prior to gasification, each type of biomass requires a different kind of pretreatment. Pretreatment can be a chemical, thermal, or mechanical process, which helps to alter the physical properties of biomass and chemical composition making it more suitable for conversion.

Once the biomass becomes available, it is usually dried and the wood chips are pulverized so that the particles in the gasifier have the greatest possible surface area and the smallest possible volume. A process that lowers the O/C ratio of biomass is known as torrefaction,[16, 17] which comprises thermal pretreatment of wood by temperature ranges of 250–300 °C under atmospheric conditions in the absence of oxygen. Prins *et al*.[18] studied the possibility of more efficient biomass gasification *via* torrefaction in different systems: air-blown circulating fluidized bed gasification of wood, wood torrefaction and circulating fluidized bed gasification of torrefied wood, and wood torrefaction integrated with entrained flow gasification of torrefied wood. The main idea behind combining biomass torrefaction and gasification is that the heat produced during gasification in the form of steam is recovered for application in the torrefaction stage. The high fuel quality of torrefied biomass makes it particularly suitable for cofiring in power plants and as an upgraded feedstock for gasification.

Up to now gasification of biomass has been tested up to industrial scale in various reactors, but its use today in long-term operations is limited. The preparation and input of the feedstock as well as the monitoring of the ash behaviour constitute the greatest challenges. Due to the stage of development in this area, which is not very advanced, there is a great number of different versions in terms of the reaction engineering.[19] Key differences include the gasification temperature and the type of biomass used (with/without preliminary treatment). Fixed-bed reactors are not suitable for synthesis gas production due to the high amounts of by-products formed and the critical scale-up. Examples of overall processes with high-temperature gasification in an entrained-flow reactor are Bioliq (Karlsrure, Germany)[20] and Chemrec (Sweden);[21] examples of methods with gasification in a fluidized bed include allothermal gasification with a solid heat transfer medium in biomass power plant Güssing (Austria)[22] and bubbling bed from Uhde, a ThyssenKrupp company (Germany).[23] Uhde has been selected as technology supplier and engineering partner by VärmlandsMethanol for a Biomass-to-Methanol (BtM) plant with an annual production of 100 000 tonnes of fuel grade methanol from biomass (forest-residue). The world's first full scale BtM plant will be strategically located in the forest-rich province of Värmland, in Hagfors, Sweden. Several companies are working on the development of adapted syntheses for methanol or dimethyl ether, *e.g*., Bioliq,[24] BioDME,[25] and Tigas.[26]

The company Lurgi (Germany) once came to the conclusion that based on extensive and in-depth studies, wood is the least expensive energy carrier for the provision of fuel gas, reducing gas for the iron-producing industry, and synthesis gas for methanol production and the rest of the C_1 industry. In the US in particular, work on the chemical processing of wood is stimulated by the fact that waste wood with a volume of more than 500 million tonnes (dry product) is generated there every year.

On the other hand, almost 3.5 billion people live in developing countries.[27] There is an ever-growing number of people in desperate need of wood for meeting their most basic personal needs: for cooking, heating, light, *etc*. These people have to spend an ever-increasing part of their work capacity just on procuring fuel. Particularly since the strong increase in crude oil prices, wood has become the alternative of choice. Due to the inadequate infrastructure, the problem of over-exploitation of traditional fuels cannot be solved by oil imports at reduced prices, as was formerly assumed.

Wood is an important economic factor, particularly in many countries in the tropics. For the rural population in the tropics (as well as in the moderate climate zones), it constitutes an important source of income. Over-exploitation is a severe threat to the existing tropical rainforests. Every year, 20 million hectares of wood are irretrievably lost in these countries due to erosion and loss of humus — an amount that is equivalent to around three times the wooded surface area in Germany. In Africa alone, reforestation would have to be increased 15-fold in order to secure the supply of wood required by the population.

India, too, has experienced a catastrophic reduction of the forest. The sub-continent currently has more than one billion inhabitants, and the number is increasing strongly. In 1880, 60% of the surface area of India was covered by forest. By 1960, this portion decreased to 25%, and today it is down to 10%, which is an an ecological disaster.

Indonesia has a high rate of deforestation: According to data provided by the FAO, in the period from 2000 to 2005, the net surface area of forest lost amounted to approximately 1.8 million hectares, an area equivalent to the surface area of Saxony (see Ref. 1, p.17). The net increase of the wooded surface area in China during this period of time amounted to approximately four million hectares per year.

According to the FAO, the majority of the global loss of tropical forest is being caused by shifting cultivation and utilization for firewood. In 2000, the latter accounted for approximately 83% of the wood cut in tropical countries. To protect the tropical rainforests, various environmental protection organizations co-initiated the so-called FSC (Forest Stewardship Council) certification, but a protection seal alone cannot guarantee ecologically responsible and socially sustainable forest management.

With regard to Brazil and the USA, many people believe that the global demand for fuel can be met with biomass, primarily wood. A number of companies have built or are building plants to prove biomass to methanol production technology. For example Range Fuels (USA) is currently building a plant in Georgia to convert wood waste into syngas and then into a mixture of methanol and ethanol, Chemrec (USA) plans to build a plant in Michigan to convert black liquor into methanol and dimethyl ether, and Methanex (Canada) has a joint development agreement with a Brazilian company to evaluate conversion of sugar cane bagasse, tops, and leaves into methanol.[28] This is certainly not applicable for Europe.

The countries with the greatest percentage of forest in Europe are Finland, Slovenia, Sweden, and, some distance behind, Austria. The largest forest surface areas (absolute values) are located in Sweden (approximately 28 million hectares), Finland, Spain, France, and Germany. Switzerland, Austria, the Czech Republic, Slovakia, and Slovenia have the largest average resources of wood per hectare at their disposal, while Germany has the largest overall wood resources in Europe, with more than 3.4 billion solid cubic metres (followed by Sweden, France, and Finland) (see Ref. 29, p. 182).

In Germany, the amount of wood cut increases continuously. A new all-time high was reached in 2007 with 76.7 million solid cubic metres.[30] This value includes trunk wood (46.8 million solid cubic metres) and pulp wood (29.9 million solid cubic metres). At 21.2 million solid cubic metres, Bavaria's portion of cut wood is the largest. Nevertheless, the chances of the construction of 1000 tonnes per day plant for wood-based methanol in Europe are considered to be very small because the wood production surface area required for this purpose would be 1 500 km^2.

In summary, it can be said that wood regained importance as a raw and work material in the beginning of the 21st century, as it can be produced in an almost CO_2-neutral manner, it is compatible with an ecological and sustainable economy, it can be processed with little energy, and it is recyclable in its entirety.

III. Biogas

Biogas as feedstock for the production of methanol can be obtained by the fermentation of biomass in biogas plants. Suitable basic materials for the technical supply of biogas foremost include the following biological resources:

— fermentable, biomass-containing residues such as biological waste, food residues or sludge;

— farm fertilizer (liquid manure);

— unused plants and plant parts (such as catch crops, plant residues and the like);

— energy plants cultivated for this purpose (regenerative feedstocks).

A large part of the feedstocks mentioned above, in particular farm fertilizer, plant residues and energy plants, is produced in agriculture. Therefore, this sector has the greatest potential for biogas production.

Biogas is generated through the natural process of anoxic microbial decomposition of organic material. In this process, micro-organisms convert the carbohydrates, proteins and fats contained in the material into the primary products, methane and carbon dioxide. The process consists of several steps, each being accomplished by micro-organisms with various types of metabolisms. Polymeric components of the biomass, such as cellulose, lignin or proteins, are first converted into monomeric substances (of low molecular weight) through microbial exoenzymes. Substances of low molecular weight are degraded to alcohols, organic acids, carbon dioxide, and hydrogen through fermenting micro-organisms. The alcohols and organic acids are converted into acetic acid and hydrogen through acetogens. In the last step, methanogenic archaea convert carbon dioxide, hydrogen, and acetic acid into two final products: methane and water.

The gas mixture, which is saturated with water, is composed mainly of methane (45% – 70%) and carbon dioxide (25% – 55%). Traces of nitrogen (0.01% – 5%), oxygen (0.01% – 2%), hydrogen (0% – 1%), hydrogen sulfide (10 – 30 000 mg m^{-3}) and ammonia (0.01 – 2.5 mg m^{-3}) are usually present in the mixture as well. As indicated in Table 2, different feedstocks produce different yields of biogas and, according to their respective composition, gas mixtures with varying methane content.

Table 2. Comparison of biogas feedstocks.[31]

Feedstock	Biogas yield in m^3 per tonne of fresh weight	Average methane content (%)
Maize silage	202	52
Grass silage	172	54
Whole-plant rye silage	163	52
Fodder beet	111	51
Biological waste	100	61
Poultry manure	80	60
Sugar beet chips	67	72
Pig manure	60	60
Cattle manure	45	60
Distillers' grains	40	61
Liquid pig manure	28	65
Liquid cattle manure	25	60

Prior to its utilization (feeding into the natural gas network) or processing (production of synthesis gas), the raw biogas has to be subjected to a complex conditioning process. In addition to the removal of water, hydrogen sulfide and carbon dioxide from the biogas, its heating value must be adjusted to that of the natural gas in the respective gas network (conditioning). Due to the high technical effort, the conditioning process is currently profitable for only very large biogas plants.

In the period from 1999 to 2010, the number of biogas plants in Germany increased from approximately 700 to 5905, and they generate approximately 11% of the power from renewable energy sources. By the end of 2011, this number is expected to rise to 7000 plants.[32] Due to the tendency to build larger plants, the installed capacity increased at a higher rate and reached 1270 MW in 2007. The approximately 9 billion kWh of power generated in 2007 accounted for 10% of all power generated from renewable energy sources and 1.5% of the total power demand in Germany. It is expected that the production of biogas can be increased to 12 billion m^3 of biomethane per year by 2020. This corresponds to a five-fold increase of the capacities in 2007.[33]

In parallel to the utilization of conditioned biogas in the energy sector as discussed above, the interest in biomethane as feedstock for the production of methanol has also continued to grow.[7, 34, 35] In this respect, taken into account was the fact that the feedstock used can be subject to significant differences in quality due to the different biogas pathways and depending on various influencing factors (*e.g.*, substrate used, biogas conditioning procedure used, reforming conditions, *etc.*), which is highly significant for the economic and ecologic evaluation of the product methanol.

According to the current state of the art, two concepts for the provision of biomethane from biogas prevail. Both concepts are divided into two stages: (1) raw biogas production and (2) biogas conditioning. Raw biogas production comprises the preliminary treatment (including ensilage, storage and substrate treatment), the fermentation (wet fermenter with secondary fermenter, the gas reservoir, a condensing boiler for heating the fermenter), and the processing of the fermentation residues. The biogas conditioning stage comprises the drying, the desulfurization, the methane enrichment, and the pressure adjustment.

The substrate used in both types of plants is composed of different amounts of liquid manure, regenerative feedstocks, and residues. Liquid manure in this case means liquid cattle manure. The regenerative feedstocks used consist of an established mixture of maize silage, whole-plant silage, and grains. Both concepts reflect the current state of biomethane production and produce 250 m^3_N of biomethane per hour. They differ in respect to the fermentation substrate and the methane enrichment method. For the first concept, liquid manure and regenerative feedstocks are used in equal amounts. The methane enrichment in this concept is carried out by means of pressure swing adsorption, the procedure that has been used most often in Germany so far.

As a second concept for the production of biomethane, a typical plant for the utilization of regenerative feedstocks, as they were built frequently in the past years, was examined. This plant is supplied with a mixture of 90% regenerative feedstocks and 10% liquid cattle manure. The altered composition of the substrate in this concept results in a higher specific power demand (with reference to the amount

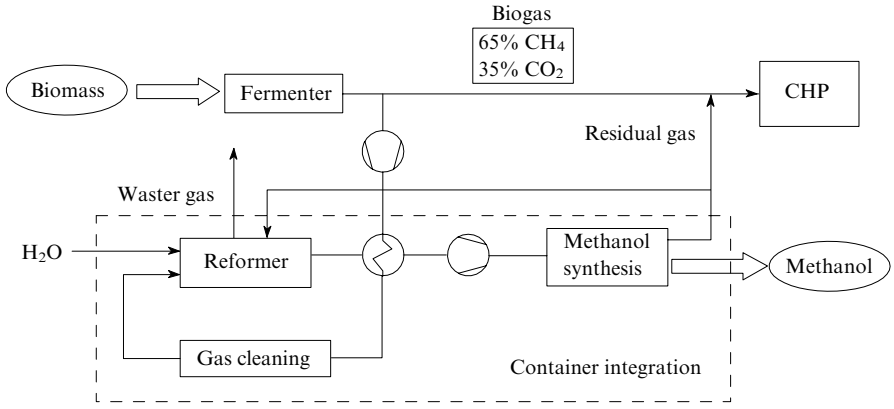


Figure 4. Schematic flow diagram of methanol production from biogas based on the 'once-through' concept without carbon dioxide separation.[6] (CHP are combined heat and power supply systems).

of substrate input) due to the more complex loading process. On the other hand, the demand for thermal energy for preheating the substrate decreases due to the higher energy density of the regenerative feedstocks. Preheating the substrate is necessary in order to avoid disturbing the sensitive fermenter environment (37 °C).

This concept uses pressurized water scrubbing instead of pressure swing adsorption for methane enrichment. This technology has been used in Europe for a long time, and it is mainly employed in large new plants. The biomethane produced in this way and purified to the quality level of natural gas is fed into the natural gas network or used for the production of methanol. The material flows required for economic and ecologic evaluation were accounted for on the basis of the method and data used by Althaus *et al.*[36]

Figure 4 illustrates the schematic flow diagram of the demonstration plant for methanol production from biogas as designed and operated by the Centre for Solar Energy and Hydrogen Research (ZSW) in Stuttgart.[6]

By means of anaerobic fermentation of sludge, biogas containing ~65% methane and ~35% carbon dioxide is produced and used as fuel gas in a combined heat and power plant (CHP). For methanol production, a part of the biogas is channelled off, cleaned in a gas filter, heated and desulfurized. The water vapour required for the reforming process is injected into the biogas flow before it enters the reformer. In the reformer, a synthesis gas is produced that contains a high proportion of carbon dioxide in addition to hydrogen and carbon monoxide. After the water is condensed out of the product gas and separated, the synthesis gas is converted into raw methanol under 5–8 MPa pressure and a temperature of 250–280 °C. As the synthesis gas produced from biogas is not suitable for the recycle loop without a separation of CO_2, the facility is designed according to the 'once through' concept, which is simpler in terms of processes. For example, the synthesis gas can be used within the process for the operation of the reformer or in the power plant.

IV. Carbonic acid

Carbon dioxide is a natural component of the air; its current average concentration is 0.039 vol.% (390 ppm) (see Ref. 1, p. 20). At the same time, it is an important part of the global carbon cycle. Carbon dioxide is produced both inside living organisms as a by-product of cellular respiration and during the combustion of carbon-containing substances with sufficient supply of oxygen. Plants, certain bacteria and archaea reconvert carbon dioxide into biomass through fixation.

Carbon dioxide exists in the atmosphere, the hydrosphere, the lithosphere and the biosphere and ensures an intense exchange of carbon between these geospheres. Figure 5 illustrates the average global tropospheric carbon dioxide distribution. The atmosphere contains approximately 700 gigatonnes of carbon in the form of gaseous carbon dioxide. The hydrosphere contains approximately 38 000 gigatonnes of carbon in the form of dissolved carbon dioxide as well as dissolved hydrogen carbonates and carbonates. The lithosphere contains by far the largest portion of chemically bound carbon dioxide. Carbonate rock such as calcite and dolomite contains between 20 000 000 and 60 000 000 gigatonnes of carbon (see Ref. 37, p. 159 and then).

Anthropogenic carbon dioxide emissions, *i.e.* those caused by mankind, amount to approximately 36.3 gigatonnes per year and constitute only a small part of the total carbon dioxide produced from mostly natural sources (~550 gigatonnes per year).[38] Approximately half of the additional carbon dioxide is absorbed by the biosphere and the oceans. The other half of the emitted carbon dioxide remains in the atmosphere, resulting in a measurable increase of the concentration. This fact causes numerous complex problems. Carbon dioxide is a component of many natural gases and has to be extracted from them, usually prior to gas transport. For example, Alaskan gas contains approximately 20% CO_2, and in some offshore gases the content is even higher. CO_2 is produced in every combustion process, but its extraction as a raw material for chemical

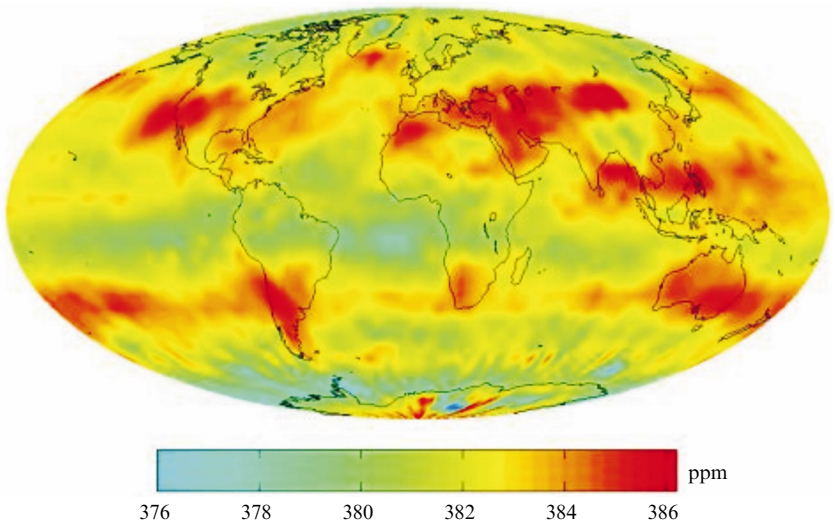


Figure 5. Global carbon dioxide distribution in the troposphere, recorded by NASA's Atmospheric Infrared Sounder (AIRS) in July 2008 (http://photojournal.jpl.nasa.gov/catalog/PIA11194).

utilization is limited from a technical point of view and is not profitable from an economic point of view.

The situation is different for auto-thermal partial oxidations of coal, peat, wood and crude oil residues for the production of synthesis gas for methanol synthesis and Fischer–Tropsch synthesis, and hydrogen for ammonia synthesis and for direct hydrogenation of coal. In this case, CO_2 is formed twice, first in the partial oxidation for heat supply, and again in the conversion reaction for hydrogen enrichment or its purification. This usually results in a CO_2 content of 32% to 36% in the total gas. In the production of synthetic natural gas, or SNG, the volume of CO_2 is even twice as high with reference to the amount of methane used.

If hydrogen was available at a low price, this simple-to-produce, pure, sulfur-free carbonic acid could be used as a basic material for methanol synthesis. The processes required are known: they have already been technically implemented and produce an extremely pure product. But when the fossil resources decrease further or become more expensive, or if they even run out—which could happen in 150 to 200 years, depending on the population—only carbonic acid dissolved in the air and the water will remain as a resource for the organic chemical industry, apart from biomass.

However, if its mobilization is not too expensive, carbon dioxide can be used by means of methanol as a universal chemical and energy feedstock. Binding carbon dioxide by converting it into methanol would be all but an ideal solution, creating a cyclic process like the cycle of production and decomposition of biomass that has existed for aeons.

Therefore, the issue that needs to be discussed is how to isolate carbonic acid in the most cost-efficient way possible and which CO_2 sources are available for this purpose from a technical and economic point of view. Table 3 shows which carbon resources are available in the world as a whole.

CO_2 can be extracted from the air by means of absorption or adsorption processes in combination with the corresponding desorption methods. For example, absorption can be carried out with water-carbonate solutions, amines, methanol, lime water, *etc*.[39] At the Brookhaven National Laboratory in Upton, NY, Steinberg and his staff worked on the relevant problems early on by way of detailed studies and numerous publications.

The higher concentration of CO_2 in the deeper layers of the oceans, which constitute a large carbon dioxide well, is particularly interesting. According to estimates, the oceans contain more than 50 times more carbon than the atmosphere.

The energy efficiency for the expulsion of carbonic acid from sea water is approximately 21%. On the other hand, the efficiency of the pressure absorption of carbonic acid from air into water and the subsequent desorption is only 0.8% (For comparison: oxygen and nitrogen can be separated from the air by means of liquefaction with an efficiency of 10%). The CO_2 dissolved in the oceans is not only in balance with the atmosphere, but also with the dissolved carbonate and bicarbonate. Extraction from the sea water would result in a gradual decrease of the CO_2, and it would take many years to reestablish a balanced state.

The situation is different with the combustion of fossil resources for power generation or coal gasification and steam reforming of natural gas, in which great amounts of very pure carbon dioxide are produced as only one product of the water-gas shift reaction in the production of synthesis gas (see Ref. 40, p.13 and then). Economically acceptable and ecologically optimal solutions are required for the separation and storage of this carbon dioxide for the purpose of its subsequent utilization. The objective is long-term security, *i.e*., a status or state that ensures that the stored carbon dioxide can be retained in the carbon dioxide reservoir in its entirety and for an indefinite period of time, while taking the necessary precautions against negative effects on people and the environment into account (CO_2 sequestration). The main area of application of this Carbon Dioxide Capture and Storage system, or CCS, is planned to be the climate-friendly utilization of fossil resources for power generation in power plants. If biomass was used as a fuel in combination with CCS, carbon dioxide could be withdrawn from the atmospheric cycle. However, large-scale utilization of this system in power plants seems possible in 10–20 years at the earliest (Ref. 41, p. 205 and then). On the other hand, for the capture and storage of carbon dioxide from natural gas, two large-scale CCS projects have already been realized in Europe, and one has been realized in North Africa.[42]

Geological formations such as non-recoverable coal seams, completely exploited salt deposits, depleted oil and gas fields as well as profound saline aquifers are particularly considered to be possible CO_2 reservoirs. Deep sea storage is not excluded either. The exchange of methane hydrates in sediment layers at the bottom of the ocean with CO_2 has been studied since 2008.[43] At the level of the EU, geological storage of carbon dioxide is regulated by the Directive 2009/31.[44]

Table 3. Global carbon resources in 10^9 t (see Ref. 1, p. 21).

Organic sources	Estimated amounts	Inorganic sources (CO_2)	Estimated amounts
Plants	830	Atmospheric	683
Onshore rock	1500	Fresh water	330
Oceanic rock	1000	Sea water (surface)	500
Oceanic biomass	2	Sea water (deep water)	35 000
Oil and natural gas	550	Carbonates in the sea	3000
Coal	5700	Solid carbonates	20 000 000
Peat (USA)	120		
Oil sand and shale	43 000		

Another possibility of sequestration is offered by afforestation, which, according to Hüttermann and Metzger,[45] would be more sensible and could be realized at a significantly lower cost than the separation of CO_2 from exhaust gases. In sustainable forestry, the carbon stored in the wood is withheld from the atmosphere over a long period of time. If the wood is not used, for example in a natural or primary forest, the stored carbon is returned to the atmosphere as carbon dioxide through the decomposition of the trees. After its useful life, the wood can continue to be used as a carbon reservoir through recycling, or the stored energy can be used by way of combustion, producing exactly the same amount of carbon dioxide that was withdrawn from the atmosphere as the wood grew.

In addition to the capture and storage of carbon dioxide, research is also going in the direction of the conversion of carbon dioxide produced by the combustion of fossil energy carriers into new energy carriers, increasing the added value if possible. For example, carbon dioxide can be converted into methanol, formic acid or synthetic natural gas (SNG) using hydrogen (from regenerative sources, if possible) and suitable catalysts.[4,46] Japanese scientists have developed a catalyst for the conversion of carbon dioxide and hydrogen into methanol, which offers a conversion capacity that is two to three times higher than that of customary catalysts.[47] The process requires cheap hydrogen that has to be produced by means of electrolysis of water using power generated from regenerative energy sources.

V. Waste and sludge

Thus far, waste and sludge have not been used for the production of synthesis gas, although the volume of this kind of waste material is very large (see Ref. 1, p. 20). Of the 455 kg of waste per capita produced in German households in 2009, 199 kg were household waste and bulky waste, 143 kg were recyclable materials, and ~111 kg were biological waste.[48] In the European Union, the amount of biological waste produced per year totals 118 to 138 million tonnes. This amount is expected to increase by 10% until the year 2020, reaching an annual amount of ~680 kg per European citizen.[49] The economically and ecologically optimal disposal of waste, therefore, constitutes one of the greatest environmental challenges for waste management in the 21st century.

Current European legislation (Directive 2008/98/EC) defines the hierarchy of the objectives of waste management in detail, according to a basic principle: avoid rather than recycle (recycling, reutilization or energetic utilization) rather than dispose. As an overall principle, the most environmentally friendly solution prevails.[50]

As biological waste is biomass, its large-scale recycling and energetic utilization is of primary interest. Wet materials can be used in biogas plants; dry materials can be used for direct combustions or recycling, *e.g.*, conversion into BtL (Biomass to Liquids) fuel, including methanol. A method that has been used particularly in the US for decades is the milling of the biological household waste on site.[51] The biological waste is milled down to small particles by means of a garbage disposal unit and flushed together with the waste water to the sewage treatment plant.

In Germany, sludge amounted to approximately 2.2 million tonnes (dry mass) with a calorific value of 10470–18840 kJ kg^{-1} in the past years. This corresponds to an energy equivalent of approximately one million tonnes of hard coal. Depending on its subsequent utilization, the sludge has to be pretreated in different ways. Several sequential procedures have to be carried out: drainage, thickening, conditioning and drying.

Sludge is rich in nutrients because the bacteria use the substances in the water for the formation of biomass in the biological stage. Nitrate, phosphate, and other nutrient salts are of particular importance for agriculture. Due to the high ratio of organic substances (~50%), sludge can be used as a fertilizer in order to improve the humus balance of the fields.[52]

Sludge that is not used as a fertilizer is utilized in thermal processes (combustion, gasification, or carbonization).[53–55] A sufficient heating value can be reached by prior drying, which, however, requires a high amount of energy. In order to improve the energy balance for the energetic utilization of sludge, only co-firing in power plants or waste incineration plants fuelled with solid materials is possible. In rare cases, so-called mono-gasification of the 'dry' sludge is used for the production of fuel gas for combined heat and power plants.

The so-called hydrothermal carbonization of the sludge, which makes it possible to utilize almost the entire amount of carbon contained in the biomass for fuel or synthesis gas production (similar to the BtL process) is particularly interesting.[56] The process is based on slow pyrolysis, excluding the air oxygen, which decomposes the biomass into volatile components and carbon. Furthermore, oils are produced that polymerize and carbonize as well. In the exothermal reactions of hydrothermal carbonization, approximately 3/8 of the heating value of the biomass (with reference to the dry mass) is released (with high proportions of lignin, resin and/or oil, this ratio is still at least 1/4). If the process is designed in a smart way, this waste heat could be used to convert wet biomass into dry bio-char, and possibly to utilize part of the converted energy for power production. This way, the process of hydrothermal carbonization would make it possible to store permanently large quantities of carbon all over the world, in a decentralized way, for subsequent recycling or energetic utilization.

Waste and sludge can also be used together with light agglomerating hard coal or brown coal as fuel. For example, sludge and municipal waste are briquetted together with light agglomerating coal and then gasified in the traditional way. The large amount of cellulose in the waste facilitates the utilization of the coal, which otherwise cakes. Co-incineration of brown coal and sludge is being carried out by BASF. The sludge is drained by means of the Carbo-Sed process developed by BASF.[57] With the 'Simplex process', very cheap gas is produced from 50 tonnes of sludge, 5 500 tonnes of municipal waste and 7 000 tonnes of coal; after an appropriate cleaning process and thermal-catalytic treatment, this gas can be converted into methanol synthesis gas.

VI. Conclusion

The principle of material utilization of renewables as part of the closed cycle of biosphere is the embodiment of sustainable chemistry. Methanol production from such materials as well as the following methanol-tree have *per se* environmental advantages over identical products which are based

on fossil fuels like crude oil, natural gas, or coal. Actually, the refinement of alternative resources for the methanol economy is geared to basic principle of the classical crude oil refineries. For this reason methanol as universal chemistry and energy raw materials come to the view of many scientists and users. Nevertheless, the supply of the chemical industry with this raw material exposes very strong by changes in the energy market. Therefore, it is very important to design selective catalytic processes which would use the total potential and advantages of renewables.

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