

## 6 Renewable carbon-based transportation fuels

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Approximately 11% of the world-wide primary energy consumption of ca. 420 EJ/a, corresponding to about 45 EJ/a, is covered by biomass today. The energetic use of biomass can be increased in the future by a factor of 2 to 3. With the assumption that 50% of the biomass available for energy purposes is employed for fuel generation, approx. 10% of the present EU-15's fuel consumption for transportation may be substituted by bio-fuels. Taking into account the increased agricultural areas of the EU-27, this potential appears substantially higher, approx. 20%. The world-wide potential is estimated at approx. 30%.

Due to the limited availability of agricultural area, an important selection criterion for future fuels is the specific fuel yield per hectare cultivated area. The specific fuel yield differs substantially and ranges between approx. 11 MWh for bio-diesel made from rape-seed and 40 MWh for hydrogen from miscanthus (per hectare and year). Considering an average mileage of 12000 km, one hectare cultivated area can currently supply fuel for 1.2 vehicles (assuming bio-diesel from rape-seed and the present average fuel consumption of 8 l-diesel-equivalent) or 11 vehicles in the future (hydrogen from miscanthus, 3 l-diesel-equivalent).

The conversion technologies leading to high yields per hectare are fermentation processes for the production of methane-containing product gases (substitute natural gas, SNG) and thermo-chemical gasification processes for the production of hydrogen and synthetic fuels from synthesis gas. However, thermo-chemical conversion is still in a developing stage, whereas production technologies of bio-ethanol, bio-diesel and bio-gas are state-of-the-art. Depending on the availability of the technologies, first priority will be given to renewable fuels which are compatible with the current fuel supply and distribution infrastructure. In the short term, these are as a neat fuel (100%) and/or as a blend, as well as ethanol and/or the octane booster ETBE (Ethyl-Tertiary-Butyl-Ether) added to gasoline. In the medium term, possible renewable fuels are Fischer-Tropsch hydrocarbons (e.g. gasoline and diesel substitutes), methanol, dimethyl ether (DME) and SNG. Hydrogen will possibly become a generally accepted fuel in the long term only, due to its specific infrastructure requirements.

Hydrogen produced with renewable electricity may contribute substantially to the renewable fuel generation in the future, as it is not subject to the availability limitations of the biomass resources. Electrolytic hydrogen can be used directly as transportation fuel, or together with CO<sub>2</sub> or biomass for the synthesis of carbon-based fuel. Due to the competition between the direct consumption of electricity and its use for electrolysis, electrolytic hydrogen will be only a long-term option.

## 6.1 Introduction

The production and utilization of renewable fuels<sup>1</sup> are key aspects for power supply and road transportation in the future. About 20% of the total anthropogenic carbon dioxide emissions are attributed to transport-related CO<sub>2</sub> emissions and the current trend indicates that the world-wide share will continuously increase with economic growth [99Wal]. The reduction or stabilization of the transport-related greenhouse gas (GHG) emissions to the current level must involve a significant reduction of the GHG emissions per vehicle kilometer in a short-term action (increase the powertrain efficiency) along with long-term measures involving the gradual introduction of renewable fuels. Comparing the costs for avoiding carbon dioxide emissions, it appears more advantageous to substitute fossil fuels with renewables in the electricity and heat generation sector than in the automotive sector. However, the evaluation results can shift in favor of automotive fuels once the diversity and supply security criteria for fuels are taken into account.

On the one hand, the transportation sector generates a high share of the CO<sub>2</sub> introduced into the atmosphere. On the other hand, exhaust gas pollution from traffic has a high local impact, especially in congested urban areas. Besides increasing the efficiency and decreasing the emissions of conventional combustion motors, a fundamental modification of the fuel supply must occur in the long term which avoids both global climate-relevant effects and local pollution impacts. For this purpose new drive technologies (e.g. fuel cells) as well as the further developed conventional combustion motor concepts must be introduced which can be supplied with an increasing proportion of regenerative fuels in the long term. A further motive for introducing regenerative alternatives in the fuel market is the almost complete dependency of the transport sector on crude oil. While both the electricity and the heat requirements are met by a wide mix of primary energy sources, the fuel production for transportation in the EU-15 is almost exclusively dependent (over 99%) on crude oil.

Whereas a multitude of options are available for the production of heat and electricity from renewable energy sources, the options for C-based fuels for transportation are limited. Among the various possibilities to supply these fuels, only the production from biomass comes into question in the foreseeable future – due to the availability of the organically bound carbon and for economical reasons. Besides the biogenic resources, regenerative electricity and CO<sub>2</sub> as a “raw material” (e.g. from air or exhaust gases) will only be available in the very long-term future for the production of fuels which are not subject to a limitation of resources.

So far, however, the development of renewable energies for the transportation sector has attracted little interest in the energy-political discussions. The few exceptions are e.g. bio-diesel in Germany and ethanol in Brazil. Besides these fuels, however, a number of other carbonaceous compounds which can be produced from regenerative resources are potential candidates: methanol and dimethyl ether, as well as liquid and gaseous hydrocarbons like synthetic gasoline/diesel fuels and methane-containing gases.

The question of whether and how renewable energies, in particular biomass, can be utilized in the transportation sector and which regenerative fuel is the most suitable depends on various boundary conditions which cannot be conclusively evaluated yet. The costs of avoiding CO<sub>2</sub> during the production of biogenic fuels are significantly higher than those for the generation of electricity and heat from biomass. Furthermore, due to the relatively high CO<sub>2</sub> emissions from electricity generation from fossil fuels (especially from coal), producing regenerative electricity from biomass avoids significantly more CO<sub>2</sub> than using the biomass to produce transportation fuel. For the reasons mentioned above, and due to the limitation of resources, there will be competition between the uses of biomass. The question at this point is the degree of significance which will be attributed in the future to a diversification with respect to the raw materials base in the fuel market and the related security of supply. The further progress in the market share of regenerative fuels will depend decisively on the answers to these questions.

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<sup>1</sup>) "Renewable fuels" or "regenerative fuels" are defined as liquid or gaseous energy carriers produced from renewable primary energy resources and preferably used in the transportation sector. In contrast to regenerative fuels, "alternative fuels" can be produced from either fossil or renewable primary energy sources. Further items and abbreviations used in the text are listed in [Sect. 6.8](#) (glossary and abbreviations).

In order to increase the share of alternative and regenerative fuels, a framework was set by European policy which will decisively affect the market penetration of these fuels. The European Union target quotas until 2020 [01EUC] for the share of alternative fuels in the entire fuel market for the transportation sector are represented in Table 6.1.1.

Enormous efforts are required in order to achieve these high shares, and thus the choice of the “right” fuel path is of considerable importance. The most promising options for regenerative fuels, their properties and production paths, as well as the primary energy potentials and costs, will be described within the scope of the present contribution. In consideration of international efforts toward the reduction of GHG emissions, technologies for the production of renewable carbon-based fuels are analyzed in the frame of this technical survey. Furthermore, the potentials of the renewable energy resources, the synthesis pathways, and their technical feasibility will be discussed.

Biomass is the most promising source for non-fossil, carbon-based fuels. Using biomass as feedstock, there are several methods of fuel generation:

- Extraction of bio-oil from oil plants;
- Fermentation of starch-rich and sugar-rich crops or cellulose materials to ethanol;
- Anaerobic digestion of biomass to a methane-containing bio-gas;
- Gasification of biomass and subsequent fuel generation from synthesis gas;
- Direct conversion of the feedstock to hydrocarbons or to bio-oil.

Fuels generated from synthesis gases have the highest potential with regard to a wide range of feedstock availability. This route corresponds to the entire use of the biomass feedstock. Therefore, special attention will be focused on the synthesis gas route in this contribution. Furthermore, hydrogen from renewable electricity combined with CO<sub>2</sub> as a carbon source will also be considered for renewable carbon-based fuel generation.

**Table 6.1.1.** Target quotas for alternative fuels in the European Union.

	2005	2010	2015	2020
Biogeneous fuels	2%	6%	7%	8%
Natural gas	0%	2%	5%	10%
Hydrogen	0%	0%	2%	5%
Total	2%	8%	14%	23%

## 6.2 Renewable fuels

### 6.2.1 Fuel options

The potential for alternative fuels in the automotive sector is being debated at present by both automobile producers and the oil industry. Besides gasoline and diesel, there are several other fuels which come into question for the transportation sector. There is a general agreement that in the long-term perspective (> 20 years) hydrogen has a high substitution potential. However, due to a diversification of the fuel market and the lack of an infrastructure for hydrogen, a number of carbon-based renewable fuels will be principle candidates as well. Which regenerative fuels will most likely be able to substitute gasoline and diesel for transportation purposes depends on the following criteria:

- Resource availability for the production of fuels;
- Security of supply / Diversification of resources;
- CO<sub>2</sub> and other pollutant emissions (of the entire system chain, “well-to-wheel”);
- Local emissions (especially in high-traffic urban areas);
- Infrastructure and on-board storage requirements / Vehicle complexity;
- Cruising range of vehicle without refueling;
- Energetic efficiency of the entire system chain;
- Fuel yield per agricultural land area;
- Fuel production costs / CO<sub>2</sub> avoidance costs;
- Suitability for different drive systems (combustion engine, fuel cells, as a neat fuel or blended);
- Social acceptance, Safety, Toxicity, and Environmental impact;
- Employment effects.

The only biomass-based fuels for transportation purposes which are produced today in larger amounts are vegetable oil methyl-esters (e.g. in Germany rapeseed methyl ester, RME) and ethanol (e.g. in Brazil from sugar cane, in USA from corn). We will briefly outline these fuels in the following. Afterwards, we will describe other, less-common liquid and gaseous alternatives to mineral-oil-based fuels: hydrogen, methanol, dimethyl ether (DME), synthetic liquid hydrocarbons and substitute natural gas (SNG). The most promising options for neat fuels, fuel blends and their utilization are listed in [Sect. 6.7.1](#).

### 6.2.2 Liquid renewable fuels

#### 6.2.2.1 Ethanol

Currently, ethanol is the most significant biogeneous fuel world-wide. Brazil is the largest ethanol producer and user in the transportation sector with the “ProAlcool” program. In 2001, ca. 12 billion liters of ethanol were produced in Brazil, corresponding to ca. 12% of the total Brazilian fuel requirement for transportation [\[02BEN\]](#). Ethanol is also produced in the USA as a fuel additive. The production in 2001 amounted to ca. 7 billion liters, corresponding to approx. 1.5% of the gasoline sales in the USA in the same year. The world-wide ethanol production in 2001 amounted to 19 billion liters [\[01Ber\]](#).

Ethanol is produced from sugar or by converting starch crops into sugars. The sugars are fermented into ethanol, and then the ethanol is distilled into its final form. Besides starch crops, sugar cane and sugar beet are the most frequently used feedstock for ethanol production. The production of ethanol from biomass which does not contain sugar or starch would lead to a breakthrough for a wide range of production

for this fuel. However, the cellulosic and lignocellulosic materials hydrolysis process, the first step in the production process, is not yet ready for commercialization [e.g. [00Lin](#), [00Kli](#)].

Ethanol can be used as an additive to standard motor fuels (e.g. E5: 5 vol-% ethanol in gasoline) without requiring adjustments to the infrastructure or vehicles. All the gasoline sold in Brazil is E22 and all gasoline cars in Brazil are able to use it. Even higher ethanol concentrations (E85) or pure ethanol are in principle suitable for internal combustion engines. However, the combustion motors must be modified in this case. The fuel type is automatically recognized in E85-capable vehicle concepts, and the motor control parameters are automatically adjusted. This feature allows the use of both conventional fuels and E85. A further exploitation path for ethanol is the production of the antiknock additive ethyl tertiary butyl ether (ETBE), which can be added up to 15 vol-% to gasoline.

#### 6.2.2.2 Bio-diesel and vegetable oils

Bio-diesel (FAME, fatty acid methyl ester) is an ester that can be made from several types of oils such as soybean, rapeseed, palm, or sunflower, and also animal fats. Through a process called trans-esterification, organically derived oils are combined with an alcohol (ethanol or methanol) and chemically altered to form fatty esters such as ethyl or methyl ester. The biomass-derived ethyl or methyl esters can be blended with conventional diesel fuel or used as a neat fuel (100% bio-diesel) in many diesel motors existing today. The non-esterified oil (SVO, straight vegetable oil) can only be used in specially adapted motors.

Currently, only rapeseed methyl ester plays a role in the utilization of biogeneous fuels in Germany, the largest bio-diesel producer world-wide. In 2003 bio-diesel had a 0.9% share of the entire fuel market (gasoline, diesel, and aviation fuels) in Germany, amounting to a 2.2% share of the diesel fuel market [[04Sta](#)]. Bio-diesel is available at over 1700 public fuelling stations today and is the only regenerative fuel which is currently available all over Germany. Only about 40% of the bio-diesel is sold by fuelling stations, the majority (60%) is sold to vehicle fleet operators in the transportation and freight industry.

The bio-diesel industry in Germany can look back on a positive development over the past years. Besides the tax-policy framework, the further development prospects for bio-diesel will be determined by the technical specifications for motors and emissions. Bio-diesel must rise to the technical challenges presented by the European legislation which is intensifying the legal emissions specifications as a prerequisite to the type registration for the corresponding motors. The currently valid limits can still be met without additional technical measures. In the future, however, the vehicles must meet the legal emissions requirements Euro IV and Euro V [[06DIE](#)]. Due to the future emission limits, which will not be easily met in alternating diesel/bio-diesel operation, a distribution channel as an additive to diesel fuel (up to 5 vol-% FAME) will be preferred.

Due to the low yields per area, the bio-diesel and vegetable oil fuels only have a limited substitution potential and, besides mixing with diesel, should therefore be implemented where the specific ecological advantage of bio-degradability of bio-diesel / vegetable oil is valued (e.g. substituting diesel fuel in sensitive environmental areas like agriculture, water protection areas, navigation).

#### 6.2.2.3 Bio-methanol

The exploitation paths for methanol range from additives to conventional fuels to pure methanol as a fuel suitable for future fuel cell drives or also for vehicles with Otto or diesel engines. Methanol, like ethanol, can be used in both dedicated and flexible-fuel vehicles. Further possibilities are the utilization of methanol as a reactant for producing substitute diesel fuels (together with vegetable oils), producing the fuel dimethyl ether, producing hydrocarbons with the MTG process (Methanol-To-Gasoline), or producing the antiknock additive MTBE (methyl tertiary butyl ether).

Fuel cells using methanol either transform the methanol directly at the anode (direct methanol fuel cell, DMFC), or hydrogen is first produced from the methanol in a reformer before being fed to the fuel cell (indirect methanol fuel cell). The chances for methanol as a fuel will be significantly improved if the

DMFC can be successfully commercialized, since the fuel cell peripherals are much less complex than for a fuel cell drive with a preliminary reformer step.

Methanol can be made from carbon-containing materials via gasification of the feedstock. At present there is no commercial bio-methanol plant in the world, except some plants which use mixed feedstock (fossil, renewable, waste), such as the one in Schwarze Pumpe, Germany (see [Sect. 6.3.1.2.5](#)).

Compared to conventional fuels, methanol has a decisive disadvantage: although methanol is liquid, its corrosive properties prevent distribution using the existing infrastructures (fuel stores, pipelines, etc.).

#### 6.2.2.4 Synthetic diesel/gasoline fuels

Liquid hydrocarbons offer the great advantage that they can be distributed using conventional transport systems without any restrictions and can therefore be immediately integrated into the existing infrastructure. Synthetic liquid hydrocarbons can be produced in the short term from natural gas with GTL (Gas-To-Liquids) processes and in the medium term from biomass using BTL (Biomass-To-Liquids) techniques. These fuels can then be marketed either as neat fuels or as additives to conventional fuels. In the long term, it will be possible to produce adapted “designer fuels” which are free of aromatic compounds and low in olefin for use in adapted piston engines – a prerequisite for the further reduction of pollutants with combustion-type motors. Due to its paraffin-like composition, this fuel has the maximum hydrogen content and is practically sulphur-free because of the catalytic synthesis path.

The disadvantage is the production process which is more complicated than for other fuels and its only limited suitability for future fuel cell drives.

#### 6.2.2.5 Bio-pyrolysis oils

Bio-pyrolysis oil can be used as a substitute for heating oil but is not suitable as an engine fuel. The bio-pyrolysis liquid is considered an intermediate energy carrier with an increased energy density as compared to biomass. The energy vector bio-pyrolysis oil can be produced from wood in decentralized pyrolysis plants and then transported to centralized fuel synthesis plants where it is converted to synthetic fuels via synthesis gas.

The pyrolysis liquid consists of water and organic compounds that are condensed and collected after the pyrolysis step, usually after the char is removed from the hot gas and vapor stream. These liquids are very complex mixtures of molecules which are the degradation products of cellulose, hemicellulose, and lignin. The bio-pyrolysis liquids are colored dark brown and have a distinctive, smoky odor. The main product, bio-pyrolysis oil, can be obtained in yields up to 80 wt-% from dry feed. By-products are char and gases which are used within the process. The liquids are combustible and have a heating value nearly half that of a conventional fuel oil, typically 16–18 MJ kg<sup>-1</sup>. Their water content varies, ranging from about 15 wt-% to about 40 wt-%, and they are immiscible with petroleum-derived fuels. Besides water, the major compound groups are hydroxylaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics.

### 6.2.3 Gaseous renewable fuels

#### 6.2.3.1 Hydrogen

Hydrogen is an ideal fuel to supply fuel cells, but also for conventional energy converters like combustion motors, and is accessible through a multitude of fossil and regenerative primary energy carriers. For this reason, hydrogen is considered the energy carrier of the future par excellence. A detailed summary of the latest research and hydrogen technology is given in [Chap. 7](#).

The disadvantages of hydrogen are, however, the infrastructure requirements for storage and transport. A worldwide, complete replacement of conventional fuels with hydrogen is not foreseeable even in the next decades. Therefore, at least in the short-to-medium term, a solitary focus on the option of hydrogen as an energy carrier should not be pursued.

#### 6.2.3.2 Substitute natural gas (SNG)

The currently increasing prevalence of natural gas in the transportation sector is leading the way for the utilization of regeneratively produced, methane-containing gases as energy carriers. This situation is attributed to the fact that the use of natural gas for transportation allows for a diversification with respect to fossil resources in which the local emissions – especially particles – are significantly lower than for comparable diesel vehicles, and because the vehicles are commercially available. Today, over four million vehicles world-wide run on natural gas. Since the volumetric energy density of methane is more than three times that of hydrogen, it is easier to store in gaseous form and still achieves high mileage ranges. When using adapted gas motors, the advantage of methane regarding the low specific CO<sub>2</sub> emissions is readily apparent.

So far, SNG is used in only a few countries (primarily in Sweden and Switzerland) as a regenerative-based fuel in the transportation sector [\[00Wel\]](#). The fuel is processed bio-gas from fermentation processes and is available as a fuel for vehicles either directly or is fed into the natural gas supply system where it is available at any point in the system.

A further method to produce methane from biomass is the synthesis from bio-syngas or by high-pressure hydro-gasification. In the first step of hydro-gasification, the biomass is gasified (800°C, 30 bar) to produce a gas with 50 vol-% methane [\[98ECN\]](#). In a subsequent step, the carbon oxides are further methanized at a temperature of about 400°C. The SNG produced in this manner has a quality comparable with natural gas.

These options enable methane to be used as a regenerative transport fuel within the existing distribution infrastructure and without investing in the transport infrastructure required for hydrogen.

#### 6.2.3.3 Dimethyl ether (DME)

Dimethyl ether (DME) is a colorless and non-toxic fuel and the simplest of all ethers. DME, like methanol, can be produced from any carbonaceous feedstock, including biomass. Although it is a gas, dimethyl ether is handled at moderate pressures like the widespread LPG (Liquefied Petroleum Gas, propane/butane). At atmospheric pressure, it boils at -25°C and has a vapor pressure of 6 bar at 25°C (30 bar design pressure). Therefore, the LPG infrastructure can be utilized with minor modifications, i.e. ocean transport in liquid form by LPG tankers and subsequent distribution as either a refrigerated liquid or in pressurized tanks and LPG-style gas bottles.

Due to its high cetane number (55-60), DME is an excellent fuel for adapted diesel motors. The high efficiency typical for diesel motors is achieved with DME. Due to the lack of C-C bonds and the high oxygen content, the exhaust is practically free of particulates. DME is especially recommended as a fuel for heavy-load vehicle traffic, as it would require only a relatively low number of filling stations.

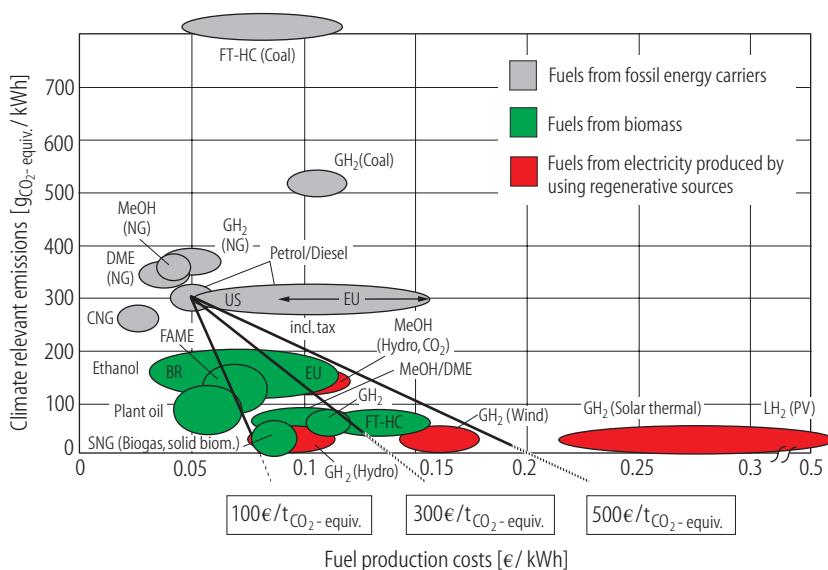


### 6.2.4 Costs and CO<sub>2</sub> emissions of renewable fuels

The implementation of regenerative fuels must take into account the cost situation along with the ecological effects. Figure 6.2.1 illustrates that, in the foreseeable future, the costs associated with the conversion of regenerative primary energy carriers into fuels will be higher than the current costs for diesel or gasoline. In general, the conversion processes used in the production of regenerative fuels are more complicated and less efficient (and thus more expensive) than the physical separation processes required for the extraction of diesel or gasoline. Furthermore, the pure raw material costs from about 0.02 to 0.03 €/kWh [04Spe] for energy plants are comparable to the crude oil costs of about 0.035 €/kWh (at 70 US\$/barrel), a drawback compounded by their much lower efficiency for conversion to fuel.

The costs for biomass-based fuels range from 0.05 to 0.15 €/kWh and are thus mostly significantly higher than the production costs for gasoline or diesel. The costs for liquid hydrogen from electricity generated by photovoltaics can amount up to 0.5 €/kWh, a price of ca. 5 € per liter gasoline/diesel equivalent.

Fuel generation is linked to various degrees of energy expenditures and environmental effects: those from the extraction of the primary energy, from the production process, from the transportation of the product, regarding the possible uses of by-products, and the fuel use itself. Renewable fuels are distinguished by their low consumption of limited resources and correspondingly low CO<sub>2</sub> emissions. Compared to the gasoline and diesel production chains, a significant reduction of CO<sub>2</sub> emissions can be achieved. The expenditures for biomass-based fuels depend primarily on whether waste materials or energy plants are utilized and how the by-products are used. Additional concerns, also for fuels based on renewable electricity, include the transportation chains and other downstream processing steps.



**Fig. 6.2.1.** Costs and climate-relevant emissions (production process and use) of renewable and fossil fuels. The lines denote the costs of avoiding CO<sub>2</sub> of 100, 300 and 500 €/tCO<sub>2</sub>-equiv.. The primary resources are listed in parentheses: PV - photovoltaics; MeOH - produced from natural gas (NG), from wood, and using CO<sub>2</sub> from power plants and H<sub>2</sub> produced by electrolysis; GH<sub>2</sub> - gaseous hydrogen at 250 bar; LH<sub>2</sub> - liquid hydrogen; CNG - compressed natural gas (250 bar); SNG - substitute natural gas (250 bar). Prices without taxes, except gasoline/diesel with and without taxes in US and EU. Reference price of crude oil: 70 US\$/barrel. Fuel production costs from biomass calculated for European conditions. Ethanol costs are also quoted for Brazil (BR) [04Spe].



Pursuant to the reduced consumption of fossil primary energy carriers, the greenhouse gases released by the production and combustion of regenerative fuels are significantly lower. While a reduction of up to 90% of the climate-relevant emissions are possible for regenerative fuels, the production of synthetic fuels from fossil primary energy carriers (natural gas, coal) lead to CO<sub>2</sub> emissions which are even higher than for conventional gasoline/diesel fuels from crude oil. In particular, the utilization of coal in the production of Fischer-Tropsch fuels causes drastically higher CO<sub>2</sub> emissions (by a factor of 2.5!). Even the production of synthetic fuels or hydrogen from natural gas, related to the secondary energy carrier produced, involves ca. 20% higher CO<sub>2</sub> emissions than for gasoline/diesel. These increased emissions must be compensated in the total energy chain (“well to wheel”) by energy-efficient drive technologies such as fuel cells.

The production of bio-diesel leads to somewhat higher CO<sub>2</sub>-equivalent emissions than one would suspect based on the energy consumption. This effect is mainly attributed to the nitrous oxide emissions resulting from the cultivation methods (e.g. fertilizer use). A considerable amount of non-renewable energy is required in the production of ethanol. The reduction of climate-relevant gases is therefore less pronounced in these cases than for the production paths over the intermediate products synthesis gas or bio-gas, or when based on renewable electricity.

The estimated cost for renewable fuels from CO<sub>2</sub> varies significantly, depending on the technology and the plant scale considered. For methanol synthesis from atmospheric CO<sub>2</sub> and electrolytic hydrogen, costs of ca. 0.15 €/kWh<sub>MeOH</sub> have been calculated for a 100 MW<sub>e</sub> hydropower station in remote areas with electricity costs of 0.025 €/kWh. If flue gas is considered as a source of CO<sub>2</sub>, the methanol production costs are around 0.1 €/kWh<sub>MeOH</sub> [98Spe1].

Compared to the reference case for gasoline/diesel in Fig. 6.2.1, the costs for avoiding CO<sub>2</sub> can be calculated from the cost difference and the reduced climate-relevant emissions for the various regenerative fuels. The lines drawn in the figure indicate the CO<sub>2</sub> avoidance costs of 100, 300, and 500 €/t<sub>CO2-equiv.</sub> over the reference case (70 US\$/barrel).

The lowest costs for avoiding CO<sub>2</sub> result from the use of the fossil resource natural gas. Natural gas exhibits lower CO<sub>2</sub> emissions per kilowatt-hour than gasoline or diesel as a result of its chemical composition. The more hydrogen contained in a (fossil) fuel, the lower the resulting CO<sub>2</sub> amount per kilowatt-hour. Natural gas is somewhat cheaper than gasoline or diesel, even in the compressed state, so that even negative CO<sub>2</sub> avoidance costs result in this case (without considering further transaction costs).

The lowest CO<sub>2</sub> avoidance costs for the production and utilization of regenerative fuels can be found for non-esterified vegetable oil and ethanol produced from sugar cane in Brazil with < 100 €/t<sub>CO2-equiv.</sub>. The average CO<sub>2</sub> avoidance costs are 100-150 €/t<sub>CO2-equiv.</sub> for bio-diesel and substitute natural gas from bio-gas or from solid biomass via gasification, ca. 200 €/t<sub>CO2-equiv.</sub> for methanol as well as for DME from biomass, and at least 300 €/t<sub>CO2-equiv.</sub> for Fischer-Tropsch hydrocarbons. The CO<sub>2</sub> avoidance costs are much higher when using electricity produced from regenerative sources, with the exception of hydrogen produced by hydropower at ca. 150 €/t<sub>CO2-equiv.</sub>. Both hydrogen from wind energy and methanol produced from hydrogen (produced by electrolysis using hydropower) and CO<sub>2</sub> (separated from the exhaust gases of conventional power plants) generate CO<sub>2</sub> avoidance costs of ca. 400 €/t<sub>CO2-equiv.</sub>. For solar hydrogen the CO<sub>2</sub> avoidance costs soar to at least 600 €/t<sub>CO2-equiv.</sub>.

At these prices, the costs of avoiding climate-relevant emissions in the transportation sector by using regenerative fuels mostly lie significantly higher than for other measures like e.g. the substitution of fossil energy carriers with biomass in the heat market (up to 50 €/t<sub>CO2-equiv.</sub>) or by using biomass for electricity generation (at 50-100 €/t<sub>CO2-equiv.</sub>). It has to be mentioned that the CO<sub>2</sub> avoidance costs for bio-fuels calculated for European conditions in Fig. 6.2.1 can be much lower for other locations, e.g. ethanol production in Brazil, where CO<sub>2</sub> avoidance costs < 50 €/t<sub>CO2-equiv.</sub> for ethanol can be achieved.

## 6.2.5 Renewable fuels today

### 6.2.5.1 Ethanol

The world ethanol production is increasing, amounting to  $29 \cdot 10^9$  liters in 2003. The major producers are Brazil and USA, but there are some interesting developments in other countries as well. In 1999 Brazil was the world-wide leader in ethanol production with  $12 \cdot 10^9$  liters, followed by USA with  $6.6 \cdot 10^9$  liters [01Ber]. In 2001, ethanol represented 42% of the total gasoline consumption in Brazil [02BEN], and 1.5% in the USA [02RFA]. However, Brazil could lose its dominant role as leading ethanol producer and user in the next couple of years, depending on the decision regarding the gradual replacement of MTBE in gasoline, and whether the commercialization of cellulose-to-ethanol production becomes viable. The discovery and production of new enzymes and the development of new processes will allow the economic production of ethanol from cellulose feedstock in the near future. A large range of biomass feedstock can be converted into ethanol, including straw, corn fiber, sawdust, paper sludge, yard clippings, and forestry waste wood, as well as dedicated energy crops like switch grass and fast-growing trees.

Besides in Brazil and the USA, new production centers could emerge in Thailand, where the ethanol production reached the level of  $0.65 \cdot 10^9$  liters by 2003, as well as in China, where the ethanol production increased up to  $2 \cdot 10^9$  liters [04IEA2]. India is the third country in Asia which has started to produce ethanol for fuel purposes. At present the ethanol production capacity in India is  $3.2 \cdot 10^9$  l/a. Figure 6.2.2 shows the world ethanol production by continents and Fig. 6.2.3 by feedstock.

There are no fixed targets for bio-ethanol in Europe, but the European Commission plans to increase the share of bio-fuels, including bio-ethanol, from at present 0.3% to 5.75% by the year 2010. Ethanol as a fuel plays a smaller role in Europe than in the Americas, but it is likely to intensify with several projects under way. Spain will become the largest bio-ethanol producer in the EU once the ethanol plant in Salamanca ( $2 \cdot 10^9$  l/a) comes on line in 2007. A second plant with a capacity of  $1.26 \cdot 10^9$  l/a has been operated in Galicia since December 2002 [04XUN]. The bio-ethanol production is also expected to increase in Germany and France in the next years.

Ethanol has the tremendous advantage that it can be mixed with conventional fuels and does not require a new infrastructure for market introduction. It will therefore play a significant role as a transportation fuel in the near-term future. Favored by their natural conditions, the Americans will continue to develop their leading position in ethanol production and Asia will experience new production growth. Even though the role of Europe as an ethanol producer and market for ethanol fuel is not yet fully defined, it is expected that the share of ethanol in the fuel market will increase in the near future.

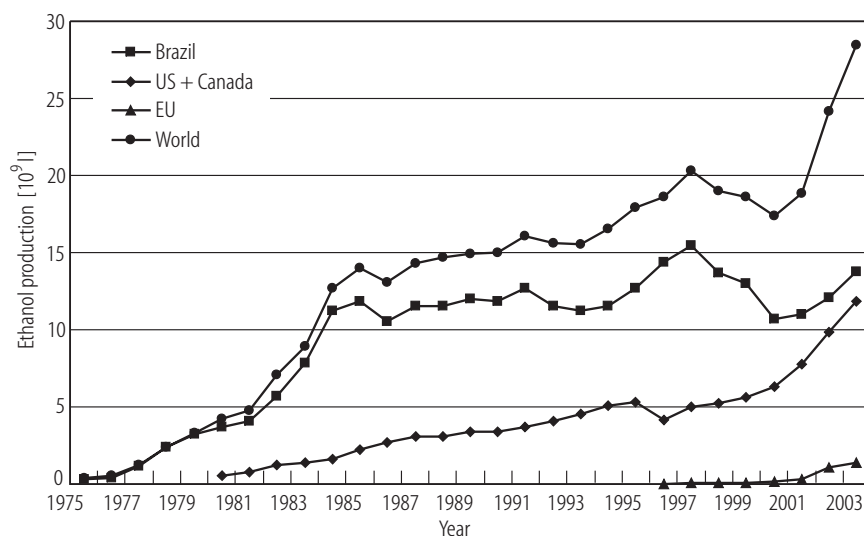
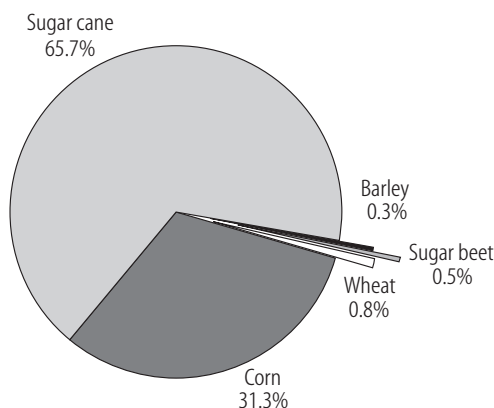
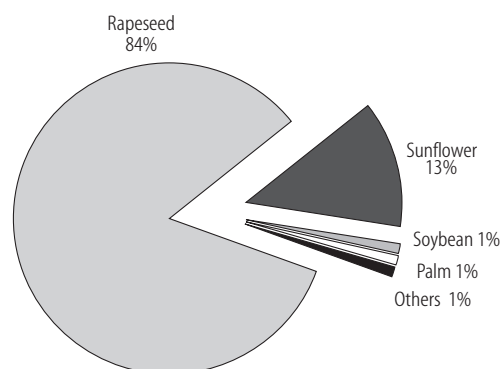


Fig. 6.2.2. World ethanol production [04IEA2].



**Fig. 6.2.3.** World ethanol production by feedstock [04IEA2, 03MET].

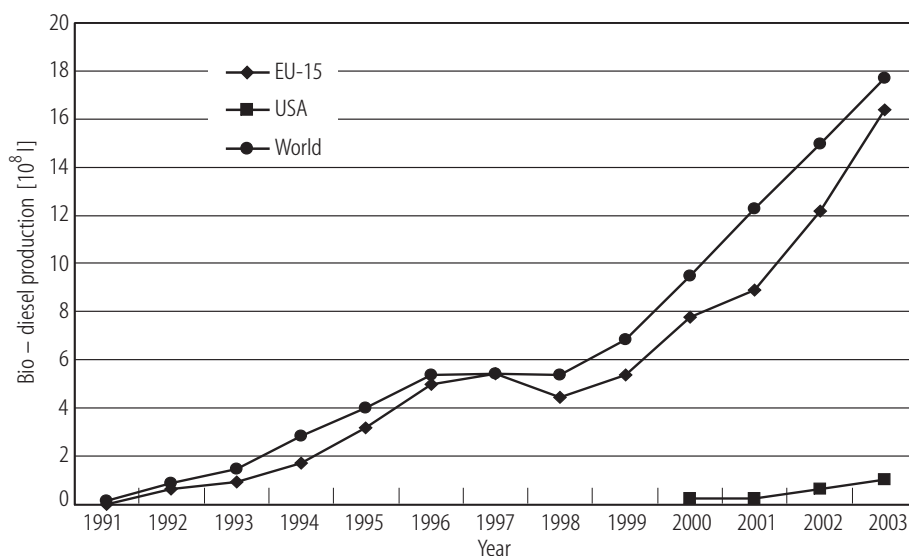


**Fig. 6.2.4.** Raw material sources for bio-diesel [03Koe].

### 6.2.5.2 Bio-diesel

Rapeseed oil methyl ester (RME) was the first bio-diesel fuel produced commercially in 1988 [01Koe]. Soon after RME was established in the market, the search for alternative feedstocks, such as waste oils, fats of animal origin, vegetable oils (e.g. palm oil, soy oil) etc. began. An appropriate blend of different fatty acid esters determines the quality of diesel, whereas the key factor for the economy is the cost of feedstock for bio-diesel. Figure 6.2.4 shows the feedstock used in bio-diesel production worldwide. Figure 6.2.5 presents the current world bio-diesel production. The present bio-diesel market is dominated by European producers and this trend will continue in the next years.

The task for marketing is to target the most profitable niches and to promote bio-diesel to the customers there. Environmentally driven regulations, e.g. emission limitations, biodegradability, zero-toxicity for water life, etc. can carve out specific market segments for bio-diesel. Other strategies include the blending of bio-diesel with conventional diesel and use as a normal diesel fuel.



**Fig. 6.2.5.** World bio-diesel production [04OER, 04Ful, 05EIA].

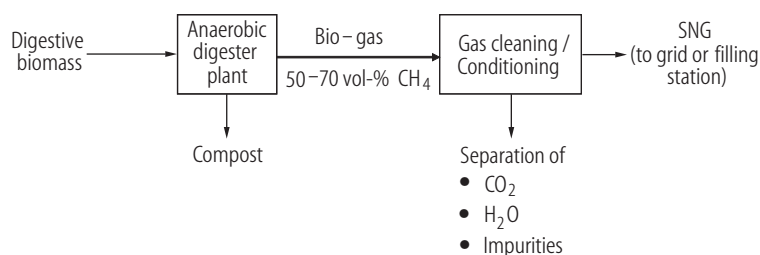
### 6.2.5.3 Bio-gas

Although bio-gas is most frequently used to produce power and heat in CHP (combined heat and power) plants, it can also be used in gas-fuelled vehicles. It is not always possible to completely use the energy content of bio-gas in a CHP plant, for example in the summer when no heat is required or in certain locations where it can be difficult to make use of the heat. Therefore, an extra bio-gas refining stage for feeding the gas into the local gas supply network and for use as a CO<sub>2</sub>-neutral automotive fuel was developed [02REN].

SNG (Substitute Natural Gas) from bio-waste via anaerobic digestion is a state-of-the-art renewable fuel production technology which is in limited use today (see Fig. 6.2.6). The raw material is bio-waste (biodegradable “green” wastes from households, industry and agriculture, e.g. wet kitchen waste, organic oils and fats, liquid manure, etc.), which undergoes anaerobic digestion. In the future, biodegradable energy plants can also be used for bio-gas production. Bio-gas from digester plants contains 50-70 vol-% methane, the rest is mainly CO<sub>2</sub> and some impurities like sulphur compounds.

The raw bio-gas is cleaned and dried, and CO<sub>2</sub> is removed from the gas. CO<sub>2</sub> can be separated by pressure swing adsorption (PSA), where the CO<sub>2</sub> in the pressurized gas is held back by an adsorption column. An alternative process design to separate CO<sub>2</sub> from bio-gas is a CO<sub>2</sub> scrubbing process with an absorption liquid. Further CO<sub>2</sub> separation technologies are membrane processes and cryogenic technologies [03Sch]. The upgraded gas consists mainly of CH<sub>4</sub>, in a quality equal to natural gas, which can be fed into the natural gas network or used directly - without long-distance grid transport - as a vehicle fuel. The quality demands made in the gas cleaning/conditioning process depend on whether it is going to be fed into the gas network or used in a local network for supplying gaseous transport fuels. SNG via digestion has all the advantages that natural gas offers (especially the emissions behavior of internal combustion engines) and can be produced on a regional scale.

World-wide only a limited number of about 30 plants have been realized for the upgrading of bio-gas. Two-thirds were erected for generating a vehicle fuel directly at the SNG filling station without gas network transport, and one-third for feeding the upgraded gas into the gas grid [00Wel]. Most of them make use of scrubbing processes and the PSA technology for CO<sub>2</sub> separation.

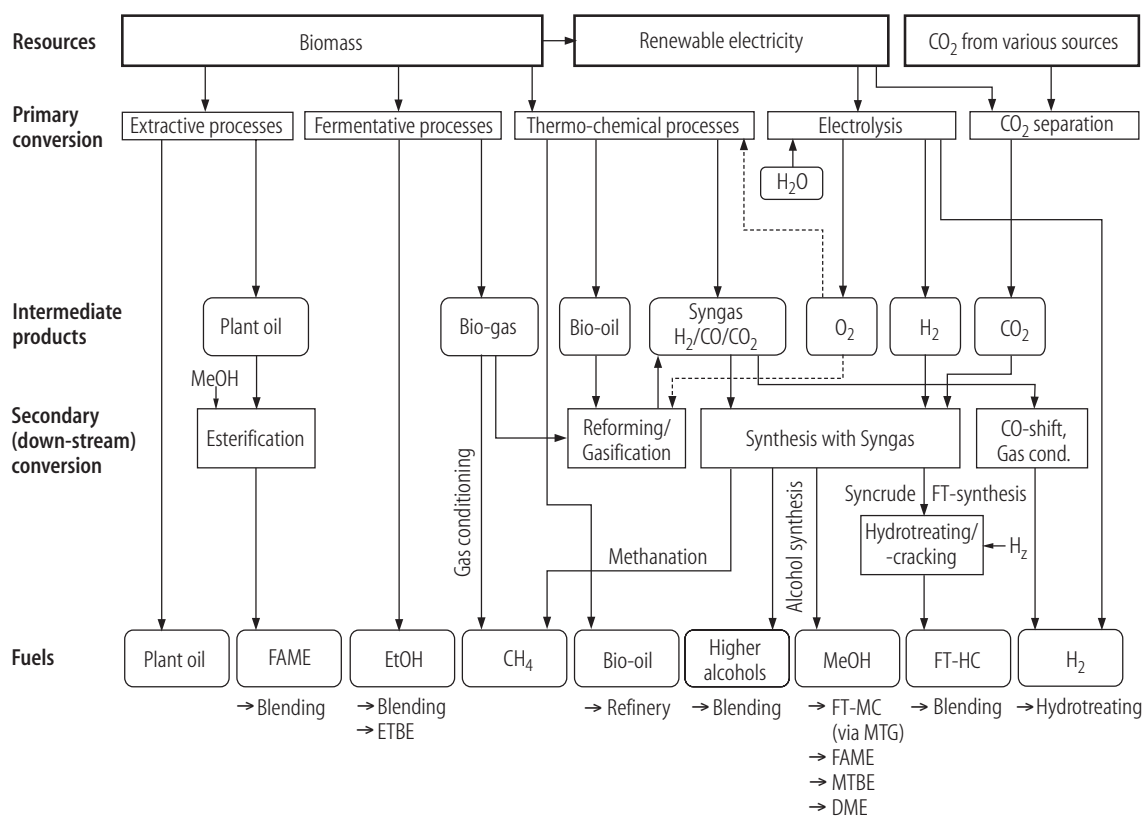


**Fig. 6.2.6.** Conversion of digestive biomass to a substitute natural gas.

## 6.3 Technical pathways for renewable fuel generation

The need to introduce renewable energies in the transportation sector will increase in the medium term. To this end, several different transformation chains are available based on electricity produced from renewable sources, biomass, or a combination of both. The main pathways for preparing fuel from renewable energy sources are illustrated in Fig. 6.3.1. The production methods can be roughly divided into extractive, fermentative, and thermo-chemical methods, as well as water electrolysis for producing hydrogen.

The production pathways for automotive fuels from renewable sources presented in Fig. 6.3.1 are characterized by material and energy fluxes. Material fluxes are biomass, carbon dioxide and water – energy fluxes are electrical energy and biomass. Each production path can be presented as a combination of material and/or energy streams with dedicated technologies. Further pathways which are currently in the fundamental research stage, e.g. hydrogen production by biological and photo-electrochemical processes, are not represented here.



**Fig. 6.3.1.** Overview of possible generation pathways for renewable fuels (see Glossary in [Sect. 6.8](#) for abbreviations).

### 6.3.1 Fuels via synthesis gas

Besides the extraction and fermentation techniques, the thermo-chemical method for utilizing biomass is particularly significant because it allows the utilization of all of the vegetable material (total plant use). Only a portion of the biomass, such as oil or starch, is used in the extraction and fermentation techniques. Furthermore, a multitude of biogeneous resources can be utilized with the production methods involving synthesis gas, thereby retaining ecological diversity. Monocultures, such as the cultivation of oil-, sugar-, or starch-containing plants, could thus be avoided. In a long-term scenario, CO-free syngas, produced from CO<sub>2</sub> and hydrogen, will be a further option for the synthesis of carbonaceous fuels – an option for which the resources are not limited.

Fuel production via synthesis gas offers the largest possible flexibility not only on the reactant side, but also on the product side. The fuels with the highest application potential in the future are those which can be produced via an intermediate synthesis gas, namely hydrogen, methanol, DME, synthetic gasoline/diesel fuels, and SNG. The technology “synthesis gas production from biomass – fuel production from synthesis gas”, however, is currently not commercially available in decentralized plants (< 50 MW). The state-of-the-art for large facilities is coal gasification, a technology which cannot be easily transferred to small, decentralized plants.

The primary step in the production of synthesis gas from biomass is the thermo-chemical conversion. Ideally, the biomass is decomposed during this step into a product gas with hydrogen and carbon monoxide as the main components and which is then suitable as a reactant gas for the production of synthetic fuels (see Fig. 6.3.1). Gasification agents can be air, oxygen, water vapor, and hydrogen (as well as partial mixtures of these gas components). The main challenge for the production of fuels from biomass via thermo-chemical gasification is the production of a “synthesis-capable” gas that must meet high specifications. The synthesis gas must be free of tar, particles, and catalytic poisons, have a low proportion of inert gas and a high hydrogen content. Previous techniques for gas production from biomass have not been optimized for the production of synthesis-capable gases, but rather for gases to be used for electricity production or combustion.

As a result from the reaction equations for the production of methanol or long-chain alkanes (from CO + 2 H<sub>2</sub> or CO<sub>2</sub> + 3 H<sub>2</sub>; see [Sect. 6.3.2](#)), a particular ratio of the gas components H<sub>2</sub>/CO/CO<sub>2</sub> must be maintained for high conversion during synthesis. The stoichiometry factor  $S$  for the synthesis gas,

$$S = \frac{p_{\text{H}_2} - p_{\text{CO}_2}}{p_{\text{CO}} + p_{\text{CO}_2}}, \quad (6.3.1)$$

should therefore be adjusted to  $S = 2$  for synthesizing methanol or Fischer-Tropsch fuels. An even higher hydrogen ratio is required for the synthesis of methane, corresponding to a stoichiometry factor of  $S = 3$ . The goal of thermo-chemical gasification for subsequent fuel synthesis is therefore to produce a hydrogen-rich, well-conditioned product gas.

One must distinguish between two basic methods of thermo-chemical gasification of biomass – autothermal and allothermal methods. In the autothermal method, the energy for the endothermal gasification reaction is introduced directly into the process through a partial combustion of the reactants (direct gasification). Oxygen (and not air) must be used for the autothermal gasification because otherwise the product gas would be diluted by nitrogen. In this case, the product gas also contains the exhaust from the partial combustion, so that the stoichiometry factor cannot be achieved despite gasification with oxygen. Therefore, either the CO<sub>2</sub> must be separated in order to adjust the stoichiometry, or only a portion of the synthesis gas can be converted to fuel and the hydrogen-poor, carbon-dioxide-rich remainder can, for example, be used for the co-generation of electrical energy. A further possibility to adjust the stoichiometry is to add (electrolytically produced) hydrogen.

Higher hydrogen ratios can be achieved with thermo-chemical gasification using allothermal processes in which the necessary process energy is externally introduced (by means of a heat exchanger or a heat carrier) into the gasification chamber (indirect gasification). The allothermal method requires a more complicated process control, but has the advantage that the exhaust from the heat-providing process is not mixed into the product gas. As a result, a gas with a higher hydrogen content of up to 50 vol-% H<sub>2</sub> is produced. However, even with the allothermal method, the hydrogen content is generally not sufficient to obtain the desired stoichiometry factor.

### 6.3.1.1 Synthesis gas production from biomass

A large effort was directed towards the development of advanced biomass gasification technologies in the last decades. The current biomass gasification technology developments are essentially based on coal gasification processes. During World War II, biomass gasification was widespread. It was primarily used to create a fuel gas e.g. in cars. After the war, however, the gasifier development stagnated for many years, until the first oil crisis. At that time, the re-discovery of the tremendous potential of biomass launched a new age for gasification [99Ree]. Several recently developed biomass gasification plants have reached the pilot scale level; however, only a few technologies have advanced to the commercialization stage so far. The biomass gasification process is quite similar to that of coal gasification, yielding in both cases a mixture of gases with the same main components. However, the composition of the resulting gases is different for biomass and coal, and the reaction conditions for biomass are milder than for coal gasification due to the higher reactivity of biomass [98Kla]. As in the case of coal gasification, biomass gasification under increased pressure conditions favors the production of methane and carbon dioxide, whereas increasing the temperature tends to increase the concentration of hydrogen and carbon monoxide. Undesirable by-products and emissions encountered in the product gas, such as particulates and tar, are the main complications for its use in downstream synthesis or electricity production. Steam is often used as the gasification agent for syngas production. Blended with oxygen or air, it promotes the formation of H<sub>2</sub> and CO. Furthermore, steam gasification contributes substantially to the reduction of tar formation. The use of catalysts (e.g. Ni) in connection with steam gasification additionally contributes to increasing the hydrogen content due to the catalytic conversion of tar [98Kla]. Using high-temperature oxygen-blown gasification, the tar content can be reduced to even lower levels. The general purity requirements for synthesis gas suitable for synfuel production are listed in Table 6.3.1.

Therefore, high-priority research efforts focus on gas cleaning and on technologies with *in situ* gas cleaning/conditioning (e.g. catalytic and thermal tar cracking), which yield synthesis-grade gases. There are several options for gasification available or in development. However, only a few of them are suitable for biomass applications for producing hydrogen and synthesis gas. Gasifiers can work either with *direct heating*, in which the biomass is partially oxidized in order to supply the heat for the gasification or with *indirect heating*, using heat exchangers or heat carriers for the heat supply. For the generation of synthesis gas from biomass, indirectly heated reactors or directly heated, oxygen-blown reactors with partial oxidation are preferred. In both cases, the product gases show low proportions of inert gas (N<sub>2</sub>) with a relatively high hydrogen concentration. Besides the operation mode of the gasifier – autothermal with direct heating or allothermal with indirect heating – the main classifications of the gasification process are the *fluidized*, *fixed-bed*, and *entrained flow* reactor type.

**Table 6.3.1.** Permissible particle, tar, alkali and sulphur content of a synthesis gas suitable for a commercial methanol synthesis process [84Bee, 94Has, 02Boe].

Component	Permissible concentration [mg/Nm <sup>3</sup> ]
H <sub>2</sub> S and other sulphur compounds	< 0.1
Particles	< 0.1
Tar	< 1.0
Alkalis	< 0.25



### 6.3.1.2 Directly heated gasifiers

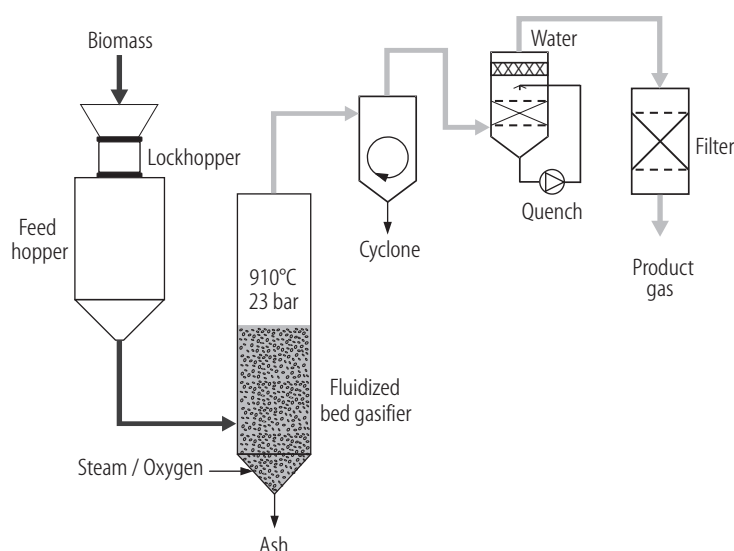
In directly heated gasifiers, the required process heat is supplied by partial combustion of the feedstock. In this case the flue gas is mixed with the product gas. Directly heated gasifiers with oxygen (or oxygen-enriched air) produce a gas with medium heating value and a lower hydrogen concentration as compared to the product gas from indirectly heated gasifiers. The inert  $N_2$  concentration is negligible when using oxygen. However, the  $CO_2$  concentration is relatively high compared to the gas from indirect heating. The operation temperatures are relatively high (900 to 1500°C).

The main advantage of these gasification processes is the low hydrocarbon concentration (short-chain like methane and long-chain like tars) in the product gas compared to gasifiers which operate at lower temperatures. Thus, an additional downstream hydrocarbon conversion (methane reforming/tar conversion) is not necessary. The disadvantage of this technique is the need for an oxygen production unit which increases the capital costs, especially due to the disproportionally high share of the oxygen plant costs for a small decentralized plant.

As the downstream synthesis plants operate at pressures of 20 to 100 bar, it is advantageous to operate the gasifier at elevated pressure. The various directly heated gasifiers developed so far, or which are still in development, differ in technical complexity, gas quality, and capital costs. Some interesting approaches with relevance for synthesis gas or hydrogen production are presented below.

#### 6.3.1.2.1 RENUGAS process

The RENUGAS process developed at IGT (Institute of Gas Technology) uses a pressurized bubbling fluidized bed reactor [91Tre]. A demonstration plant for 90 t/day of wood or 63 t/day of cane trash as feedstock was constructed by the Pacific International Center for High Technology Research in Hawaii. The oxygen requirement of the plant is about 0.3 kg/kg wood feed and the lower heating value (LHV) of the resulting dry fuel gas is 11.8-13.5 MJ/Nm<sup>3</sup>. The dry fuel gas yield is 1.0-1.2 Nm<sup>3</sup>/kg wood feed. The gasification operation temperature for wood is 910°C and the operation pressure is 23 bar. The fuel gas has the following composition: 16 vol-% CO, 38 vol-% CO<sub>2</sub>, 17 vol-% CH<sub>4</sub>, and 28 vol-% H<sub>2</sub>. A special gas cleanup system was applied in order to obtain a synthesis-grade fuel gas. A schematic flow sheet of the process is given in Fig. 6.3.2.



**Fig. 6.3.2.** Schematic presentation of the RENUGAS process [85Ger].

### 6.3.1.2.2 Carbo-V process

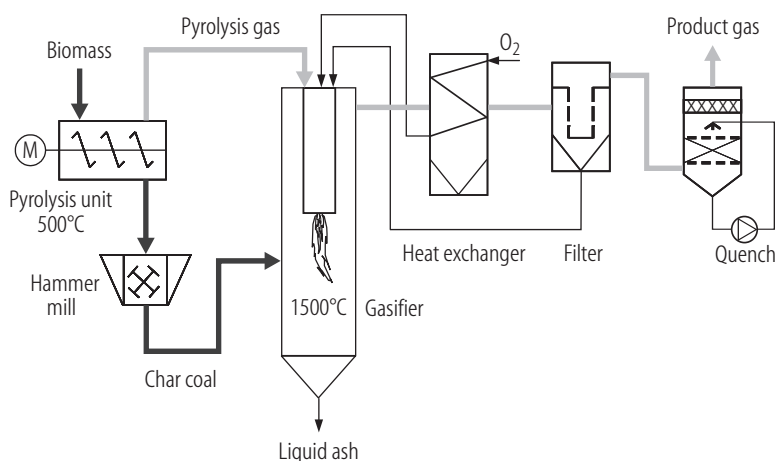
The Carbo-V process is a relatively new development from the Umwelt- und Energietechnik (UET) company in Freiberg, Germany [04Rud]. It aims to produce a tar-free synthesis gas for synfuel/hydrogen or electricity production. The Carbo-V process is a two-step process. In a first step the biomass is converted into a tar-containing gas and char coal in a pyrolysis unit at ca. 500°C. The tar-containing gas is fed into a second reactor together with oxygen as a gasification agent and used for the gasification of grounded charcoal from the first reactor. Here the char coal is completely gasified at ca. 1500°C in an entrained flow process. The ash is removed from the system in liquid form due to the high operation temperature. The process-specific advantages of the Carbo-V gasifier are:

- 1) No special requirements for the feed regarding lumpiness, homogeneity, humidity, etc.;
- 2) High operation temperature of the gasifier leads to a largely tar-free gas;
- 3) After wet cleaning, the product gas meets the high specifications for downstream synthesis or gas engines.

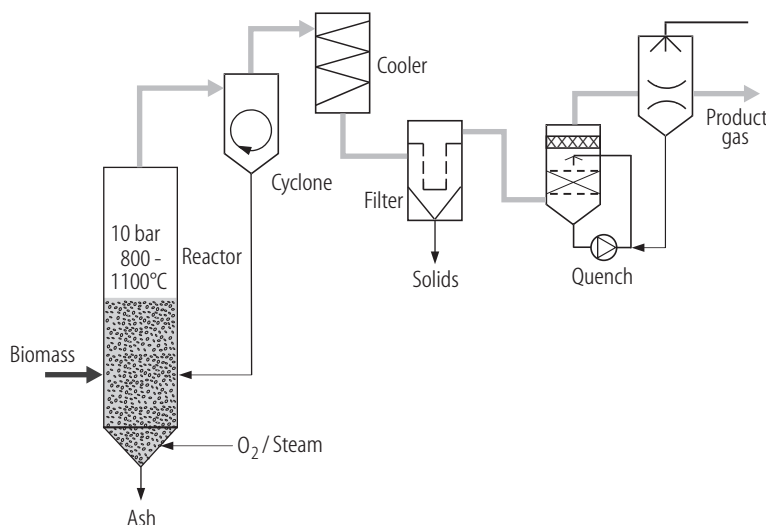
Figure 6.3.3 shows the flow sheet of the Carbo-V process. A typical product gas analysis is presented in Table 6.3.2.

**Table 6.3.2.** Typical product gas composition of the Carbo-V process.

Gas component	Gasification with oxygen [vol-%]	Gasification with air [vol-%]
CO	39.2	21.8
CO <sub>2</sub>	20.4	11.4
H <sub>2</sub>	40.2	22.1
CH <sub>4</sub>	0.1	0.0
N <sub>2</sub>	0.1	44.7



**Fig. 6.3.3.** Carbo-V process flow sheet [04Rud].



**Fig.6.3.4.** Flow sheet of the HTW high-pressure biomass/coal fluidized bed gasification [04Mey].

#### 6.3.1.2.3 HTW process

The High-Temperature Winkler (HTW) process was developed at the Rheinische Braunkohlenwerke AG, Germany, and consists of a pressurized fluidized bed reactor with oxygen/air and steam as the gasification agent. The process operates at pressures up to 10 bar and temperatures in the range of 800 to 1100°C [84Sch]. The gasifier was extensively tested between 1956 and 1964 with lignite as feedstock. A typical (steam + oxygen)/lignite ratio, e.g.  $(0.41 \text{ kg}_{\text{steam}} + 0.36 \text{ Nm}^3_{\text{O}_2})/\text{kg}_{\text{lignite}}$ , gives a carbon conversion of 96% and a carbon monoxide + hydrogen yield of  $1.4 \text{ Nm}^3/\text{kg lignite}$ . A typical dry product gas composition is: 42 vol-%  $\text{H}_2$ , 39 vol-%  $\text{CO}$ , 17 vol-%  $\text{CO}_2$  and 2 vol-%  $\text{CH}_4$ . The main characteristics of the process are

- 1) a high throughput rate,
- 2) a high-purity product gas, suitable for the synthesis of methanol,
- 3) suitability for a wide variety of feedstock (lignite, wood, biomass, etc.), and
- 4) flexibility in the product gas utilization (synthesis gas, reduction gas, hydrogen, gaseous fuel).

A demonstration plant with a production capacity of 37000  $\text{Nm}^3/\text{h}$  synthesis gas for methanol production (14 t/h) from lignite in Wesseling, Germany, was constructed in 1986. Several other feedstocks (wood, peat, etc.) were tested, obtaining a synthesis gas suitable for methanol production. Especially wood can be converted with high efficiency [04Mey].

Figure 6.3.4 shows the flow sheet of the HTW process. The raw product gas is subjected to a complex gas cleanup before methanol synthesis. The gas is separated from the solids in a cyclone and then cooled down. Downstream the gas enters a gas filter and a scrubber. Subsequently, the sulphur components are separated in a second chemical or physical washing step in order to achieve synthesis gas quality (see Table 6.3.1).

#### 6.3.1.2.4 Texaco process

The high-pressure Texaco process was developed in the eighties, based on work from the Texaco Development Corp. in the forties [89Kel]. It involves an entrained flow gasification with oxygen at high pressures (up to 80 bar) and high temperatures (around 1300°C). Due to the high gasification temperatures with the Texaco procedure, a carbon conversion close to 100% and high gas purity can be obtained. Several plants for coal gasification have been constructed in Europe and in the USA for synthesis gas production [89Kel, 87Sch1].

Texaco and HTW processes with coal gasification are highly suited for application in combined-cycle power plants [88Lam]. A 100 MW<sub>e</sub> power plant constructed in 1988 in the USA using the Texaco principle was regarded as the cleanest coal power plant in the world. The environmental and economical advantages of these gasification processes, as well as their versatility in the use of different fuels, biomass, wood, etc., were fully demonstrated in the eighties and nineties.

#### 6.3.1.2.5 Schwarze Pumpe waste-to-methanol process

At Schwarze Pumpe Spreewitz, Germany, three different types of high-temperature gasifiers for co-processing of waste (solid, liquid/paste-like), biomass (e.g. contaminated waste wood), and coal have been operating since 1998. Solid feeds are gasified in a high-pressure fixed-bed gasifier (25 bar, 800-1300°C) or in a slag bath reactor (1500-1800°C). Liquid or liquid-like wastes, such as tars, oils, slurry products (oil-water-solids), etc., are processed in an entrained flow reactor (25 bar, 1350-1800°C). The gasifying agents are water and oxygen. The product gas, after several steps for cleaning, cooling, and conditioning (stoichiometric adjustment), is supplied to a methanol synthesis plant and used for electricity generation. The share of the waste in the feed is up to 75 wt-% (rest: coal). In 2002, 300000 t of waste were processed and ca. 100000 t of methanol were produced [04But].

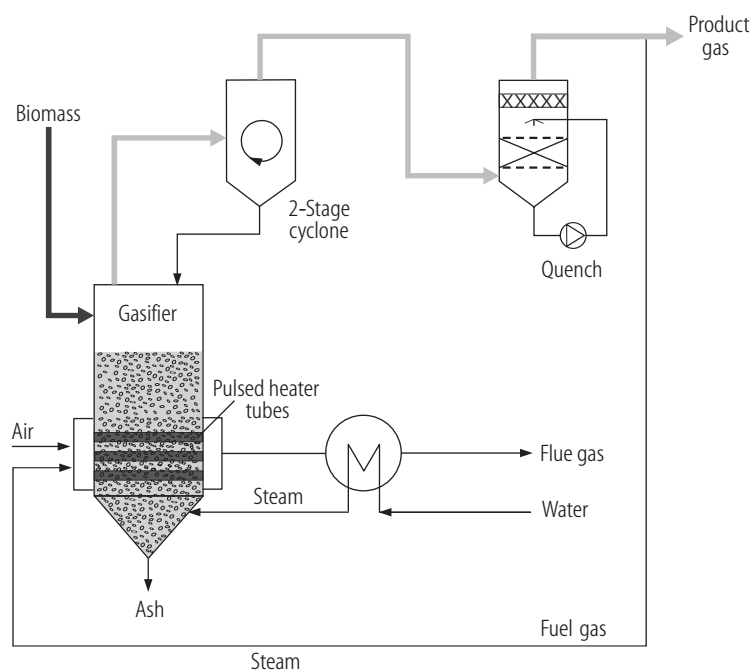
#### 6.3.1.3 Indirectly heated gasifiers

Indirectly heated gasifiers are designed to take advantage of the higher reactivity of biomass relative to coal and to produce a gas with a higher hydrogen content compared to directly heated gasifiers. A number of different technologies have been developed to the pilot stage and currently being tested world-wide. The indirect heating leads to a product gas with a medium energy content, which is not diluted with nitrogen (without the use of costly oxygen). In an indirectly heated gasifier, the heat is supplied to the reactor through a heat exchanger or heat-carrying materials like sand (allothermal process). Steam is introduced with the feedstock to the reactor to promote the gasification reaction and to increase the hydrogen yield.

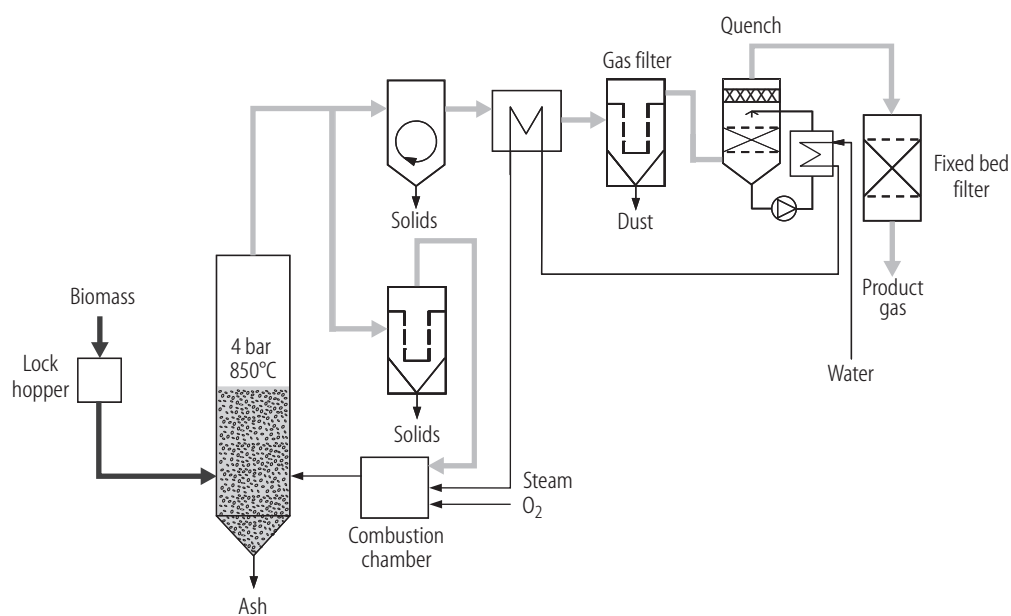
The disadvantages of the indirectly heated gasifiers for synthesis gas production are the relatively high methane and tar concentrations in the product gas due to the low operation temperature. Additionally, operation under pressure is difficult with this technology. Some of promising developments in the field of indirectly heated gasifiers for biomass are presented below.

##### 6.3.1.3.1 MTCI gasification

The MTCI (Manufacturing and Technology Conversion International) pulse-enhanced, fluidized-bed gasifier operates under atmospheric pressure. The biomass reacts with steam in a heat exchanger at temperatures of 600-730°C [90Dur]. The heat supply for the process is provided by burning some of the product gas. The novelty of the process is a pulse-enhanced combustor, consisting of compact, multiple-resonance tubes, which serves as an in-bed heat-transfer surface. The pulsed heater generates an oscillating flow in the heat-transfer tubes that results in turbulent mixing and enhanced heat transfer (three to five times higher than for conventional in-tube heating). The fuel gas / air mixture is periodically ignited. The rapid-fire pulses move through the resonance tubes at high speed, increasing the intensity of the combustion process and reducing the boundary layer thickness. The result is a more even, more efficient combustion process and an increased heat transfer to the fluidized bed [95Man, 97Hau]. A typical dry gas composition, depending on feed, is 19-24 vol-% CO, 20-28 vol-% CO<sub>2</sub>, 8-12 vol-% CH<sub>4</sub>, and 35-50 vol-% H<sub>2</sub>. The higher heating value of the product gas ranges from 12.9 to 15.9 MJ/Nm<sup>3</sup>, depending on the feed. The MTCI gasifier tolerates a large variety of feedstock (biomass, coal, straw, etc.). Different pilot plants demonstrated the process in the USA with the feed rate ranging from 9 to 13.6 kg/h [98Kla]. A flow sheet of the process is presented in Fig. 6.3.5.



**Fig. 6.3.5.** MTCI process flow sheet [95Man].



**Fig. 6.3.6.** Flow sheet of the DMT process [01HCE].

#### 6.3.1.3.2 DMT indirectly heated steam gasifier

In the indirectly heated steam gasifier developed at DMT (Deutsche Montan Technologie, Germany), the process heat needed for the biomass gasification is not supplied using a suitable heat exchanger, but rather through combustion of a part of the product gas. In contrast to other allothermal gasification processes, the flue gas from the combustion process is not separated from the product gas. This process thus leads to lower  $H_2$  concentrations and an additional  $O_2$  demand when nitrogen must be avoided in the product gas.

The gasification takes place in a stationary fluidized bed reactor at about 4 bar and 850°C (see Fig. 6.3.6). The hot product gas first enters a cyclone for dust removal, then passes through a heat exchanger where its heat is released for steam generation. Finally the product gas passes a gas filter, a water quench, and a downstream fixed-bed filter. The gas composition varies depending on whether oxygen or air is used as combustion agent. A typical product gas composition using  $O_2$  as the combustion agent is 37.5 vol-%  $H_2$ , 15.9 vol-% CO, 34.9 vol-%  $CO_2$ , 9.2 vol-%  $CH_4$ , 2.2 vol-%  $C_2H_4$ , and 0.3 vol-%  $N_2$  [01HCE].

The use of steam as a heat carrier - compared to a directly heated reactor - generates a product gas with a high hydrogen concentration as well as low dust and tar content. In order to provide the heat in the gasification zone, a part of the product gas is burned with air or oxygen. The heating value of the obtained product gas is improved when using oxygen for steam generation. The lower heating value of the product gas is ca. 10.5 MJ/Nm<sup>3</sup> if oxygen is used for the combustion process. In a pilot plant with 500 kg/h feed, the gasifier was test-operated at DMT for 27000 h in the eighties.

#### 6.3.1.3.3 DM2 staged reforming process

In the first step of the Staged Reforming Process of the DM2 Company, Germany, the biogeneous material is decomposed in a pyrolysis reactor at about 500-600°C into a gas (approx. 80 wt-%) and char (approx. 20 wt-%) [02Mue]. The heat is supplied by heat-carrying materials, e.g. metal spheres or other inert materials. The char leaves the reactor at the bottom into the firing, the gas and tars move in the opposite direction as the heat-carrying medium, entering the reforming stage and exiting at the top of the reformer, in which the organic compounds (e.g. tars, hydrocarbons) are steam-reformed to  $H_2$  and CO. The heat needed for both pyrolysis and reforming is supplied by the heat carrier which is heated up to 900-1000°C by the flue gas from the combustion chamber, where the char and residues of the feed material are burnt. The heat carrier first releases its energy in the reformer and then in the pyrolysis reactor. A schematic presentation of the process principle is given in Fig. 6.3.7.

A 1 MW<sub>th</sub> pilot plant was erected in Herten, Germany, in 2001. A feed with 30% moisture and sizes of up to 50 mm is tolerable [00Dim]. The dry gas composition is expected 56.7 vol-%  $H_2$ , 18.3 vol-% CO, 23.5 vol-%  $CO_2$  and 1.5 vol-%  $CH_4$  [02Mue]. The main advantages of the process are:

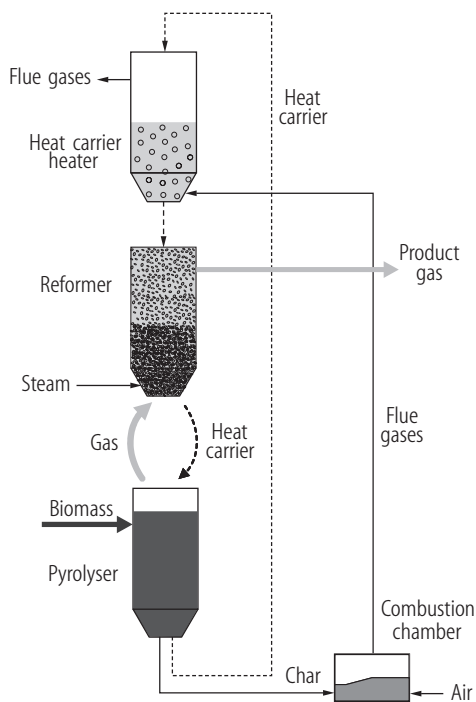
- 1) No oxygen is needed for the gasification;
- 2) Atmospheric process;
- 3) No special requirements are set for the feed material (variety of feed with a water content < 30% and size < 50 mm).

#### 6.3.1.3.4 Indirectly heated, twin fluidized bed, steam gasifier (Battelle/FERCO)

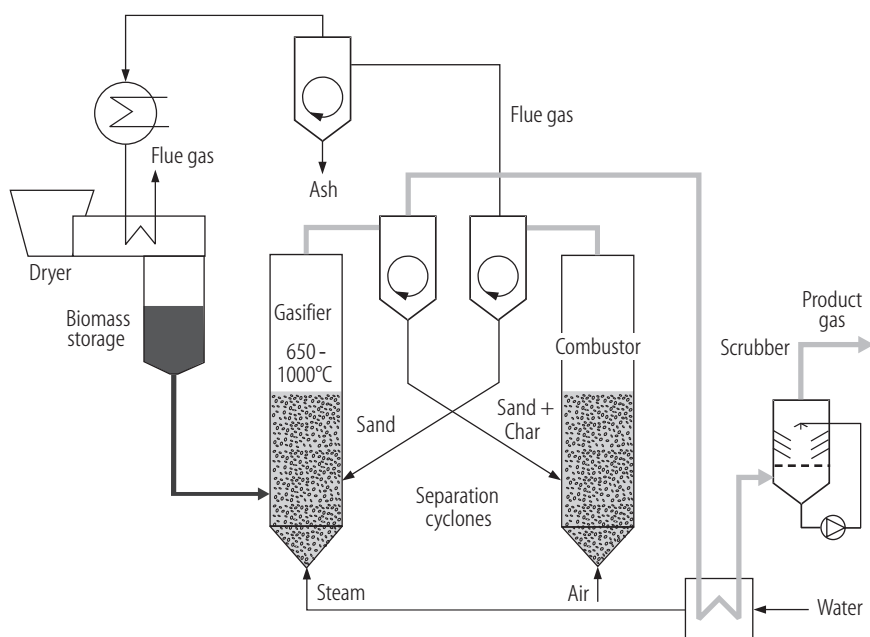
This process was developed by Battelle in the eighties and tested in a pilot plant. It produces a medium caloric gas without oxygen supply under atmospheric pressure, using twin circulating fluidized-bed gasification [92Wym]. Heat is supplied by circulating a stream of sand between two physically separated fluidized-bed reactors. Biomass enters the first reactor in which it is gasified with steam to produce gas and char (Fig. 6.3.8). A cyclone separates the gas from the sand and char, both of which enter a second fluidized-bed reactor, the combustor. The char is burned in the combustor and heats up the sand which is reintroduced into the first reactor where it supplies the heat needed for the gasification. The operating temperature of the gasifier ranges from 650 to 1000°C. The product gas is cleaned in a scrubber and the

tar thus separated is reintroduced into the combustor. The flue gas waste heat is used to dry the biomass feed. Tests have been conducted with wood throughputs of 1.5-1.7 t/h.

After successful operation of a pilot plant at Battelle, it was decided to upscale the process to a commercial scale (182 dry tons of biomass feed per day). The plant started testing in 1999 in Vermont, USA. A typical product gas composition is: 18.0 vol-%  $H_2$ , 47.0 vol-%  $CO$ , 14.3 vol-%  $CO_2$ , 14.9 vol-%  $CH_4$ , 1.1 vol-%  $C_2H_6$ , and 4.7 vol-%  $C_2H_4$ . The higher heating value of the gas is about 16.8 MJ/Nm<sup>3</sup> [00Pai].



**Fig. 6.3.7.** Principle of the DM2 Staged Reforming Process [02Mue].



**Fig. 6.3.8.** The Battelle/FERCO gasification process [00Pai].



### 6.3.1.3.5 FICFB gasification

The FICFB (Fast Internally Circulating Fluidized Bed) gasification uses the idea of a heat-carrier bed material to supply energy for gasification, somewhat similar to the DM2 process and Battelle/FERCO gasification. A heat carrier (quartz sand, catalytically active olivine) circulates between two reactors, introducing heat from the combustion zone into the gasification zone. There is no gas contact between the two zones. Biomass enters the gasification zone where it is steam-gasified. The gasification zone is fluidized with steam and the combustion zone (riser) is fluidized with air. The bed material with char moves from the gasification into the combustion zone, where the charcoal is burned with air. The exothermic reaction in the combustion zone provides the energy for the gasification via the bed material. The product gases are cooled in a heat exchanger and afterwards cleaned from dust and partly from tar with a bag filter. Tar is then separated in a scrubber with bio-diesel as the scrubbing liquid. The advantages of the FICFB process are:

- 1) Allotermal process without oxygen demand;
- 2) Compact reactor design;
- 3) Low investment costs due to the compact construction;
- 4) High energy efficiency;
- 5) Reduced tar and nitrogen content in the product gas.

Based on a 100 kW<sub>th</sub> pilot plant, a demonstration plant with the FICFB concept was erected in Güssing, Austria, with 8 MW<sub>th</sub> and an electric output of 2 MW<sub>e</sub> [00Hof, 01Hof]. The gasification temperature ranges from 790 to 900°C. A typical product gas analysis at 880°C shows the following composition: 43 vol-% H<sub>2</sub>, 30 vol-% CO, 13 vol-% CO<sub>2</sub>, 9 vol-% CH<sub>4</sub>, and 5 vol-% N<sub>2</sub>. [01Hof]. Figure 6.3.9 illustrates the reactor design for the FICFB process.

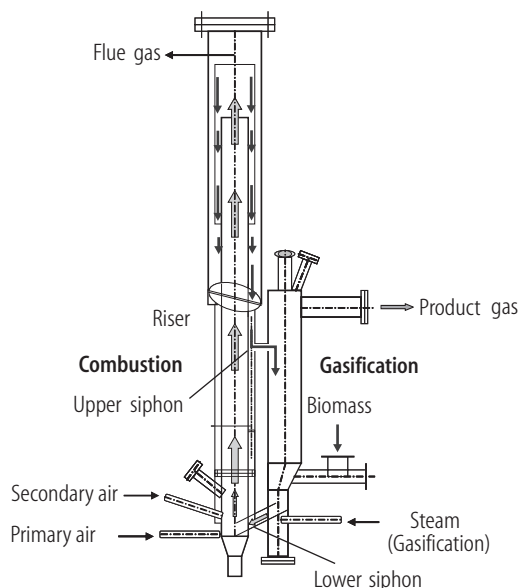
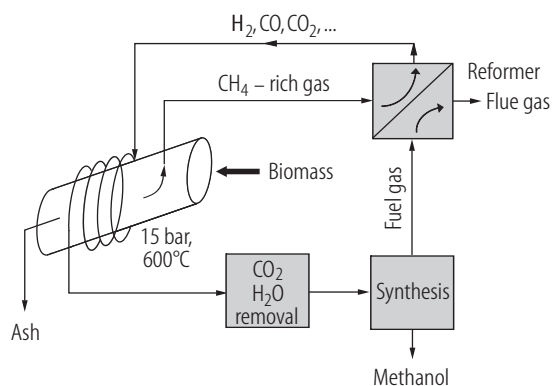


Fig. 6.3.9. FICFB gasification reactor [01Hof].



**Fig. 6.3.10.** Schematic presentation of the Wright-Malta process [91DeL].

### 6.3.1.3.6 Wright-Malta process

The Wright-Malta gasifier is specially designed for the utilization of biomass with high moisture content (typically 50%). The gasifier provides a methane-rich gas due to the combined effects of

- 1) a long residence time for the biomass in the reactor (ca. 1 hour),
- 2) high pressure (ca. 15 bar),
- 3) low reactor temperature (ca. 600°C), and
- 4) catalysis through ash recycling.

No steam addition is required due to the water content in the biomass. In the process the biomass moves through the kiln from the feed end (cool) and is gradually heated. At first, the biomass is dried, also producing steam. Then the pyrolysis yields gas, tar, and char. The gases, solids, and liquids move in a counter-current downwards, undergoing steam gasification. The hot gas moves to the cool end through coils, releasing its heat to the process. This regenerative heating and the exothermic decomposition of wood (CH<sub>4</sub> and CO<sub>2</sub> as main products) are in principle sufficient to sustain the process after an initial heat-up. Furthermore, the shift reaction which takes place is also exothermic.

Calculations show that the total heat released is apparently large enough to sustain steam gasification [98Kla]. The raw product gases then enter a reformer where the methane content is sharply reduced prior to synthesis downstream. The heat of the reformat is transferred to the gasification reactor via a heat exchanger. Including the reforming process and the methanol synthesis, an overall energy efficiency of 54% (HHV) is estimated. A typical product gas composition estimated for the dry gas downstream from the reformer is: 53.3 vol-% H<sub>2</sub>, 26.6 vol-% CO, 16.0 vol-% CO<sub>2</sub> and 4.0 vol-% CH<sub>4</sub> [91DeL]. A conceptual scheme of the process for methanol production, including biomass gasification, raw product gas reforming, and synthesis gas stoichiometry adjustment (CO<sub>2</sub> removal), is presented in Fig. 6.3.10.

### 6.3.1.3.7 Hynol process

The Hynol process was developed at the Brookhaven National Laboratory with the aim to efficiently convert biomass to methanol [94Ste1, 94Ste2]. The basic Hynol gasification process involves two main reactions: hydrogenation of carbonaceous feeds to produce methane and reforming of the methane to produce synthesis gas. Biomass is fed into a fluidized-bed reactor and reacts at 800°C and 30 bar with the excess hydrogen recycled from methanol synthesis. The methane-rich gas from the gasifier is introduced into a reformer, where it is steam-reformed to synthesis gas. Natural gas can be co-reformed in order to adjust the hydrogen content of the synthesis gas. The reformat undergoes a high-temperature cleaning, is then cooled in a heat exchanger and enters the methanol synthesis reactor. The hydrogen-rich off-gas from methanol synthesis is used as the gasification agent for biomass hydro-gasification. This Hynol process concept is presented schematically in Fig. 6.3.11.

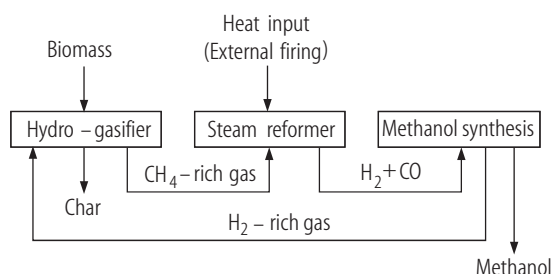


Fig. 6.3.11. The Hynol process concept.

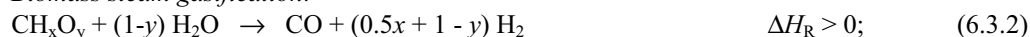
Laboratory-scale experiments performed between 1995 and 2000 [00Nor] led to the conclusion that the Hynol process can achieve a biomass-to-syngas carbon conversion of about 75%. A typical gas composition from the hydro-gasifier is: 50.0 vol-% H<sub>2</sub>, 13.5 vol-% CO, 7.5 vol-% CO<sub>2</sub>, 22.3 vol-% CH<sub>4</sub>, and 6.6 vol-% N<sub>2</sub>.

#### 6.3.1.3.8 AER process

With the AER process (Absorption-Enhanced Reforming), biomass steam gasification can continuously produce a raw gas with more than 75 vol-% hydrogen, suitable for downstream fuel synthesis or electricity production. In this approach, the CO<sub>2</sub> produced during steam gasification is separated from the reaction zone by an absorbent, so that the resulting product gas exhibits a high hydrogen concentration as well as low amounts of carbon oxides and tar [00Spe, 04Mar]. The CO<sub>2</sub> absorption shifts the reaction equilibrium towards an increased hydrogen concentration. As the reaction of carbon dioxide with the absorber is exothermic, it supplies *in situ* the heat needed for the reforming/gasification. A flue gas with increased CO<sub>2</sub> concentration is produced when the sorbent is regenerated in a subsequent process step.

The key element of the AER process is the reforming/gasification reaction in the presence of a high-temperature CO<sub>2</sub> absorbent. The absorbent consists of a metallic oxide/carbonate system, such as CaO/CaCO<sub>3</sub>. The AER process combines the reforming/gasification, shift and carbon dioxide removal reactions in one reactor, leading to a hydrogen-rich gas. The principle of the AER process is presented below with CaO as the absorbent:

*Biomass steam gasification:*



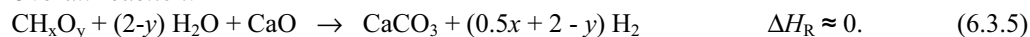
*CO-shift reaction:*



*High-temperature CO<sub>2</sub> absorption:*

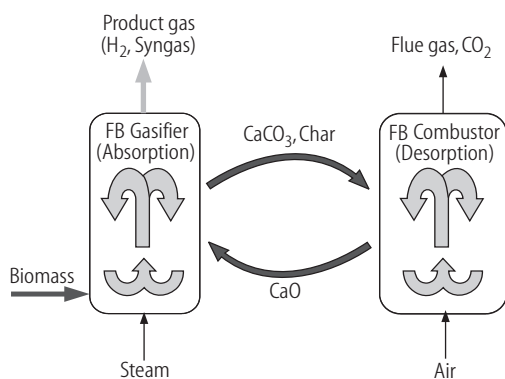


*Overall reaction:*



Depending upon the feedstock, the calculated enthalpy difference of the overall reaction can be slightly negative or zero. The process is easily adapted for synthesis gas production with a certain stoichiometry requirement by controlling the absorber amount.

In order to realize continuous operation, two fluidized-bed reactors are coupled. In the first reactor, the biomass gasification with steam takes place using absorbent as the employing bed material. The second reactor operates in the combustion mode to regenerate the sorbent (Fig. 6.3.12). In the technical realization, the reactive bed material circulates between the AER gasification reactor (600-700°C) and the char combustion reactor (800-900°C) for sorbent regeneration.



**Fig. 6.3.12.** Technical concept of the AER process for continuous synthesis gas/ $H_2$  production from carbonaceous fuels with two combined fluidized-bed (FB) reactors: a gasifier operating at 600-700°C and a combustor operating at 800-900°C.

The AER process was tested in a 100 kW<sub>th</sub> bench test plant [04Mar]. The advantages of the AER process over conventional biomass steam gasification are:

- 1) It allows the production of a product gas with a high  $H_2$  concentration (> 75 vol-%) or with a desired stoichiometry factor for downstream synthesis in a single process step;
- 2) The energy required for gasification/reforming is supplied *in situ* through the exothermic carbonation reaction of the absorber;
- 3) Reactors for downstream CO shift and  $CO_2$  removal are not required;
- 4) Tar formation is suppressed as a result of  $CO_2$  absorption and the tar-cracking properties of the sorbent.

#### 6.3.1.4 Comparison of gasifiers

Industry and a number of research institutes are active in the development of biomass gasification technologies. The focus of the R&D activities is the development of the gasifier itself and the cleaning of the product gas. The main differences between existing gasifiers for syngas production via biomass gasification are

- 1) the content of minor components in the product gas (impurities),
- 2) the content of the major components ( $H_2$ , CO, etc.), and
- 3) the necessity of an air separation plant for oxygen production.

No existing gasification technology meets all the demands to produce bio-syngas in one process step.

Air-driven, directly heated gasifiers are not suitable for synfuel generation due to the high portion of nitrogen in the product gas. Fixed-bed gasifiers are not qualified for syngas generation due to

- 1) their limited capacity range (< 5 MW) and
- 2) their disadvantages regarding the automatic control of the process.

Indirectly heated gasifiers have the great advantage of a high hydrogen content in the product gas, but the disadvantage of a high hydrocarbon content (methane and tars). To upgrade this gas to syngas quality, downstream reforming/cracking units are necessary. Entrained flow gasification shows the lowest tar content in the product gas, but it lacks high hydrogen concentrations. They require downstream shift converters, followed by  $CO_2$  removal, for adjusting the syngas. Additionally, an air-separation plant is necessary to supply oxygen as gasification agent for entrained flow gasification.

Table 6.3.3 shows the tar and particle content of the product gases in dependence on the gasifier type. As the tar formation is strongly dependent on temperature and operating conditions, the table gives large intervals for the tar concentrations. In general, high residence time, high temperature, and high steam-to-carbon ratio contribute to the reduction of the tar content in the product gas.

Figure 6.3.13 compares the product gas compositions for different gasification systems which are potentially suitable for synthesis gas production [99ZSW, 03ZSW]. Gasification processes with high hydrogen content are favorable. However, gas conditioning for adjusting the stoichiometry factor are still necessary with most gasification technologies for a high carbon conversion (with a recycle loop for the non-reacted part of the syngas). Nevertheless, the product gas composition alone is not decisive for selecting a gasification process for synthesis gas production. Besides the concentration of the main gas components and the impurities, energetic efficiency, capital costs, operation and maintenance costs and process complexity have to be considered as well.

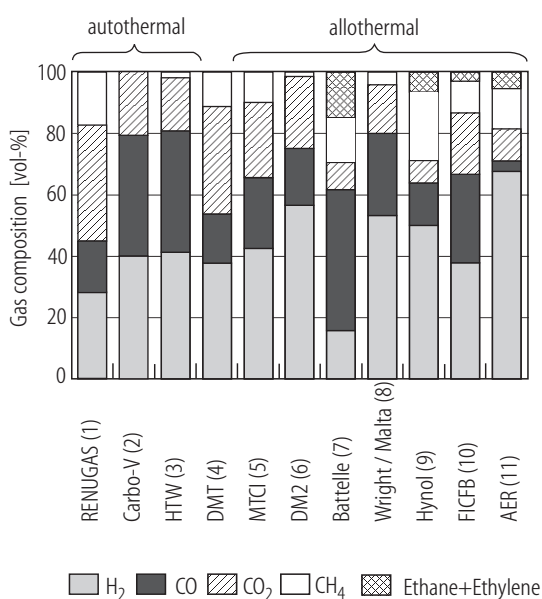
Biomass gasification has reached the point of development where first applications, such as co-firing and co-gasification, are becoming commercial. The first biomass-based IGCC plants are in the demonstration phase and will probably reach a commercial status within about 10 years. The production of liquid or gaseous bio-fuels for road transportation, via synthesis gas, can become competitive in the medium-to-long term of about 10-20 years [01Man]. However, none of the processes have been running long enough to provide reliable data on process performances and costs. The main research activities in the field of biomass-to-syngas are

- 1) development of gasification technologies with regard to the properties of different feedstock,
- 2) a gas cleaning and conditioning with regard to biomass-specific impurities like tars and alkali.

A significant amount of work must still be done before such plants could be considered for commercial syngas production applications.

**Table 6.3.3.** Tar and dust content of product gases from different gasifiers.

Gasification reactor type	Tar content [g/Nm <sup>3</sup> ]	Dust content [g/Nm <sup>3</sup> ]	Source
Co-current, fixed-bed	0.05 - 1.0	< 10	<a href="#">89Wil</a>
	0.05 - 6.0	0.1 - 3.0	<a href="#">94Has</a>
	0.1 - 2.0		<a href="#">97Bee</a>
Counter-current, fixed bed	5.0 - 10		<a href="#">89Wil</a>
Fluidized-bed	10.0 - 100	0.01 - 10	<a href="#">94Has</a>
	1.0 - 30	1.0 - 100	<a href="#">94Has</a>



**Fig. 6.3.13.** Product gas composition from different gasification technologies.

(1) [99Rec], (2) [05Olo], (3) [84Sch], (4) [97Hau],  
 (5) [95Wil], (6) [00Dim], (7) [98Kla], (8) [81Cof],  
 (9) [00Nor], (10) [01Hof], (11) [04Mar].

### 6.3.1.5 Gas cleaning

The raw product gas from a biomass gasifier contains particulates, tars, and other contaminants that may create difficulties in the downstream utilization of the gas. The concentration of these constituents depends on the reactor design, biomass feedstock, and operation conditions (e.g. temperature, pressure, etc.). For synthesis applications, the product gas from biomass gasification has to fulfill several requirements regarding cleanness (see Table 6.3.1). In general, the raw gasification product gas requires cleaning before further utilization. The primary contaminants and potential countermeasures are listed in the following sections.

#### 6.3.1.5.1 Particulates

Particulates are solid-phase materials entrained in the raw product gas stream when exiting the gasifier. They include the inorganic ash derived from the biomass feedstock, unconverted biomass in the form of char, and often reactor bed material. The particulate removal technologies vary significantly depending on the use of the product gas and include cyclones, barrier filters, electrostatic filters, and wet scrubbers.

*Cyclone filters* are able to remove the bulk particulates from the gas stream. They are particularly effective in purging large particles, removing ca. 90% of the particulates with a diameter greater than 5  $\mu\text{m}$ . Cyclones can operate at elevated temperatures to retain the sensible heat of the product gas. At lower temperatures, cyclone filters can also remove alkali and tars. Cyclones show a minimal pressure drop ( $< 0.02$  bar).

*Barrier filters* include a range of porous materials that allow gases to penetrate, but prevent the passage of particulates. They can be designed to remove nearly any size of particulate, but the pressure drop across the filter and economic constraints limit the particulate size to  $> 0.5$   $\mu\text{m}$  for gasifiers handling large gas volumes. Barrier filters are usually placed downstream to cyclones. The barrier filters include metal or ceramic rigid filters (candle), bag filters and packed-bed filters. The *rigid filters* can operate at high or moderate temperatures (400–800°C), preserving the sensible heat of the gases which is particularly important when gasifiers are coupled with turbines. *Ceramic filters* can operate at higher temperatures than metal filters, but they are susceptible to alkali and are fragile, leading to breakage under thermal stress. *Metal filters* generally operate at lower temperatures (up to 600°C) and are susceptible to corrosion, but are very stable mechanically. *Bag filters* are made of woven material, limiting the operation temperature to ca. 300°C. They are state-of-the-art and have long been used in many industrial applications. The biomass gasification gases must be cooled down  $< 300^\circ\text{C}$  prior to passing a bag filter, creating difficulties due to the presence of tars which can condense and plug the filter. In *packed-bed* filters, the gases pass through a bed with packed material such as ceramic spheres, sand, sawdust, etc. The particulates retained in the bed must be periodically removed and disposed. In big gasification plants, the accumulation of large amounts of particulates/tars can create operation problems. Packed-bed filters are currently being used in small-scale systems.

In *electrostatic filters*, the particulates pass through high-voltage electrodes that impart an electric charge to the particulates which are then discharged at collector plates and can then be removed from the plates by dry (mechanical) or wet (water) scrubbing. Dry scrubbers operate at ca. 500°C, wet scrubbers at maximum 60°C. Electrostatic filters are best suited for large-scale operation due to their high costs and huge physical size. They are rarely used in biomass gasification.

*Wet scrubbers* usually use water to remove particulates. The water is sprayed into the gas stream and the liquid droplets collect the particulates. The wet particulates are removed from the gas stream in a demister. The operation temperature of water scrubbers is limited to  $< 100^\circ\text{C}$ .

#### 6.3.1.5.2 Tars

“Tar” is a generic term for complex organic compounds that are produced during gasification. Tar in the raw product gas can create major handling problems by condensing on cold components downstream from the gasifier, plugging and fouling the contact surfaces. The tar concentration in raw gas typically varies between 1 and 100 g/Nm<sup>3</sup>. Tar removal can be carried out by physical methods or by thermal or catalytic conversion. *Physical methods* use filter or scrubbing systems (such as those used in particulate removal), operating in the temperature range where the tar is in condensed form. As the tar contains an appreciable amount of energy (up to 10% of the feed) it is preferable to preserve this energy for the product gas by converting the tar catalytically or thermally into useful products. The *catalytic conversion* of tar consists of reforming the tar using oxide or metal catalysts. The oxide catalysts, usually natural minerals such as dolomites, calcites, etc., can be used *in situ* by introducing them into the gasification reactor or a separate reactor downstream from the gasifier. This kind of catalyst usually performs the bulk removal of the tar, while metal catalysts (based mainly on Ni) are used for the deep/final cleaning [e.g. [99Cor](#), [97Azn](#), [01Ste](#)]. The operation temperature of the catalytic conversion ranges from 750 to 900°C. The *thermal decomposition* of tar is accomplished with thermal energy alone, at temperatures above 1200°C. The difficulties of attaining complete thermal cracking, along with operational and economic considerations, make thermal cracking less attractive in current large-scale gasifiers using biomass as feedstock.

#### 6.3.1.5.3 Sulphur compounds

Biomass feedstock is naturally low in sulphur and therefore sulphur removal is not necessary when the product gas is used as fuel gas. For synthesis and fuel cell applications, however, the sulphur concentration should be below 1 ppmv. In most cases, sulphur (H<sub>2</sub>S) can be removed by using low-temperature procedures (adsorption). A high-temperature (450-480°C) recovery process based on metal oxides was developed for the coal industry. The adsorption bed is regenerated externally and the sulphur is recovered. Water scrubbing can also contribute to reduce the sulphur concentration in the product gas.

#### 6.3.1.5.4 Nitrogen-containing components

In the gasification processes, the nitrogen contained in biomass is transformed into ammonia. When the gas is burned, ammonia is transformed in NO<sub>x</sub>. However, when the product gas is used for synthesis purposes or is fed to fuel cells, the ammonia should be removed before use. Catalytic destruction of ammonia is possible using catalysts similar to those used for tar conversion or hydrocarbon reforming. The ammonia conversion using Ni or dolomite catalysts is carried out at the same temperatures as those used for tar cracking. Wet scrubbing can also be used to remove ammonia in systems where a low-temperature product gas is acceptable.

#### 6.3.1.5.5 Alkali compounds

Depending on the type of biomass, the feedstock may contain significant amounts of alkali salts, particularly potassium. Potassium is an element which is required for plant growth and very high concentrations of it are present in rapid-growth biomass. Especially potassium-sodium eutectic mixtures can evaporate at moderate temperatures (650°C). Whereas particulates with alkali can be removed from the gas at moderate temperatures by filtering, the vapor passes the filter at high temperatures to condense on cooler surfaces downstream such as heat exchangers, turbine expansion blades, etc. and create serious corrosion problems. By cooling the gas before use, the alkali vapors can condense on particulates which are removed by filtration. Vapors of alkali salts are corrosive and can inactivate catalysts like those for tar cracking and for synthesis gas applications.



### 6.3.2 Fuel generation from synthesis gas

The production of synthetic fuels (“synfuels”) is a broad term for fuel generation via synthesis gas (“syn-gas”), which goes back to earlier fuel production technologies from fossil resources e.g. through coal gasification. At present, synfuel synthesis mostly refers to Fischer-Tropsch processes for gasoline and diesel fuel production and to MTG (Methanol-To-Gasoline) processes for gasoline production from methanol (Mobil technology), as well as to methanol synthesis. However, the synthetic natural gas (SNG) production can also be included with the synfuel routes. A number of R&D activities were recently launched for the production of synfuels from renewable energy sources such as methanol and hydrocarbons from bio-syngas or from renewable hydrogen and carbon dioxide [95Ban].

#### 6.3.2.1 Methanol synthesis

##### 6.3.2.1.1 Gas-phase methanol synthesis

Methanol has long been produced as a by-product (“wood spirit”) of charcoal fabrication from wood. The yields (approx. 1%) were substantially lower than for the new-generation technology route from synthesis gas. Methanol generation from synthesis gas was first carried out industrially in 1923 by BASF, Germany [98App]. The process developed by BASF is performed at temperatures of 320–380°C and pressures around 350 bar (*high-pressure methanol synthesis*). The process uses a catalyst based on  $\text{Cr}_2\text{O}_3/\text{ZnO}$ . The oxide mixture is very resistant to typical catalyst poisons in small concentrations, so that its lifetime reaches several years. Dimethyl ether, methyl formate, and higher alcohols are produced as by-products. A short gas/catalyst contact time of 1–2 s is preferred in order to suppress secondary reactions [76Wei]. ICI improved this technology by introducing a new catalyst based on  $\text{Cu}/\text{ZnO}$  [03Spa]. Copper-based catalysts are more active and more selective for methanol synthesis than  $\text{Cr}_2\text{O}_3/\text{ZnO}$  catalysts. The drawback of these catalysts, however, is their high susceptibility to poisoning with traces of sulphur compounds. Due to the high catalytic activity of copper-based catalysts, it was possible to lower the synthesis pressure to about 50–80 bar and the temperature to 250–280°C (*low-pressure methanol synthesis*). Methane steam reforming, yielding high-purity synthesis gas, finally brought great commercial success to the process. In 1966, ICI commissioned the first low-pressure methanol synthesis plant. The designed capacity of the plant of 300 t/d was greatly exceeded with a constant, regular output of over 600 t/d [98App].

Besides several technological advantages of the low-pressure process, the lower temperatures take advantage of more favorable thermodynamics. Table 6.3.4 summarizes the main features of the two processes [94Uhd, 88Cha, 99ZSW].

**Table 6.3.4.** Principal features of the high- and low-pressure processes for methanol synthesis.

	High-pressure process	Low-pressure process
Catalyst	$\text{Cr}_2\text{O}_3/\text{ZnO}$	$\text{Cu}/\text{ZnO}$
Temperature [°C]	350	220–280
Pressure [bar]	350	50–100
By-products [%]	2–5	0.2
Energy demand [MWh/t Methanol] <sup>1)</sup>	12	8–10

<sup>1)</sup> With natural gas as feed.

Modern methanol plants use a combined steam and partial oxidation reforming of natural gas for synthesis gas production, first introduced by LURGI in 1978 [98App]. This system achieves an  $S$ -value close to 2, which is not possible with steam reforming of methane ( $S$ -value for steam reforming is approx. 2.8).  $S$ , the stoichiometric factor, characterizes the synthesis gas composition, as expressed in (6.3.1). The best synthesis results can be obtained with  $S$  close to 2. The low-pressure methanol synthesis substantially reduces the energy consumption for methanol production, which is why it is presently used by most of the methanol plants world-wide. The process is very selective with regard to methanol. By-product concentrations in raw methanol, such as higher alcohols, aldehydes, ethers, esters, etc., are usually less than 0.2% (see Table 6.3.4).

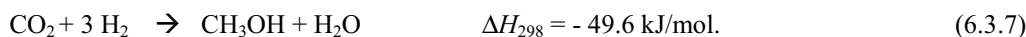
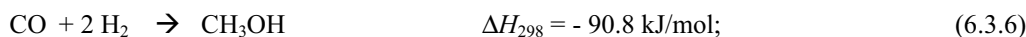
The size of methanol plants has steadily increased, reaching capacities as high as 5000 t/d today. Two methanol plants with a capacity of 5000 t/d each are on-stream in Trinidad and in Iran based on a LURGI proprietary highly efficient technology “MegaMethanol Process” since 2004/2005. The process uses an oxygen-blown, combined natural gas reformer and a cost-saving methanol synthesis plant.

In principle, the feedstock-to-methanol chain contains three main parts:

- Synthesis gas production (for synthesis gas from biomass see [Sect. 6.3.1.1](#));
- Methanol synthesis;
- Raw methanol purification (distillation).

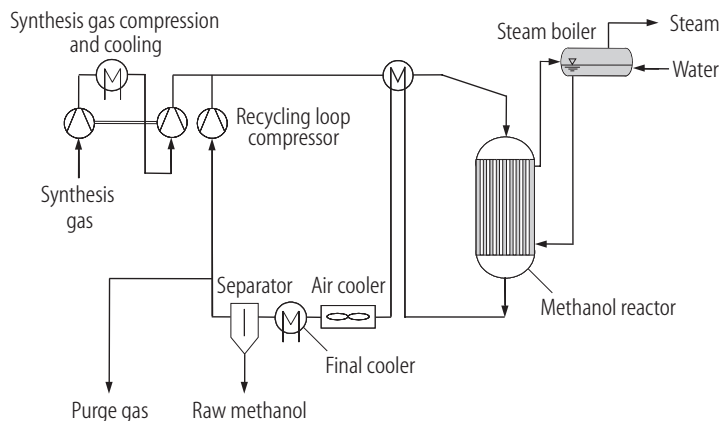
Today, methanol is manufactured predominantly from natural gas using low-pressure synthesis. Before the natural gas undergoes a reforming process (steam or combined reforming) for synthesis gas production, it must be cleaned with regard to catalyst poisons, e.g. sulphur compounds. The Cu/ZnO catalyst activity is seriously affected by even traces of sulphur compounds in the feed gas. A residual sulphur content of 0.1 ppmv can be tolerated [76Wei]. In the case of biomass as feedstock, the synthesis gas will be cleaned to remove sulphur compounds, chlorine, tars, and particulates. The desulphurization generally operates at 250–400°C or at room temperature, using fixed-bed reactors with ZnO, Fe<sub>2</sub>O<sub>3</sub>, activated carbon, etc. In case the feed contains non-reactive sulphur components, they must first be hydrogenated and then removed with the desulphurization unit.

The reactions which take place in the methanol synthesis reactor are:

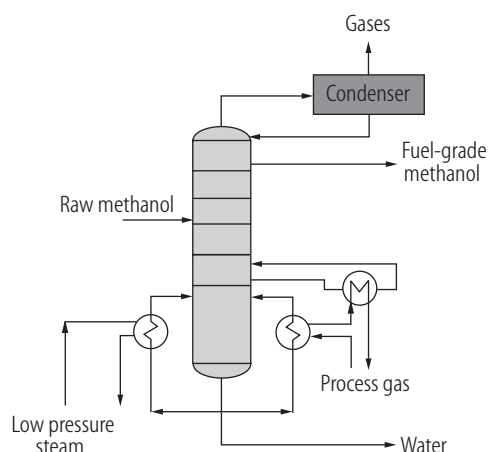


Because the reactions are exothermal and take place under volume contraction, low temperatures and high pressures favor the process. A typical methanol synthesis plant is schematically presented in Fig. 6.3.14. The synthesis reactor consists of heat exchanger tubes surrounded by boiling water. The tubes contain the catalyst. The synthesis gas enters at the top and is routed through the catalyst where the reaction occurs. The reaction heat is removed from the reaction zone by generating medium-pressure steam through evaporation of the water circulating between the tubes. The reaction products and the non-reacted synthesis gas leave at the bottom of the reactor. The tubular construction of the reactor has the advantage of rapidly removing the reaction heat and assuring a short start-up time. The reaction occurs under nearly isothermal conditions and the reactor/catalyst temperature can be easily controlled, therefore preventing the deactivation of the catalyst as a result of overheating.

Thermodynamics do not allow the complete conversion of the syngas into methanol in a single reactor pass. The unreacted gases must therefore be reintroduced into the reactor by using a recycling loop (see Fig. 6.3.14). Since the synthesis gas always contains small amounts of inert components such as methane, nitrogen, etc., their share increases during recycling and they must be purged from the synthesis gas stream. The purge gas, which possesses a considerable heating value, is used in the reforming section. The amount of purged synthesis gas is directly related to the concentration of inert components and increases linearly with it. Therefore, an excessively high share of inert components in the synthesis gas leads to a decrease in efficiency of the methanol plant. With a 4 vol-% inert share in the synthesis gas, approx. 25 vol-% of the recycling loop gas has to be purged. The maximum carbon conversion rate of a conventional synthesis gas (stoichiometric factor around 2 with ca. 6 vol-% CO<sub>2</sub>) in a once-through reaction is about 30%. Using a recycling loop, conversion rates above 90% can be achieved.



**Fig. 6.3.14.** Methanol synthesis plant with recycling loop [96Lur].



**Fig. 6.3.15.** One-column methanol distillation plant for fuel-grade methanol production.

The raw methanol contains water, dissolved gases, and a small amount of unavoidable by-products with boiling points differing from methanol. In order to obtain the desired methanol purity, the raw methanol undergoes a *raw methanol purification* including a degassing step and two distillation steps for the removal of low- and high-boiling-point by-products, respectively.

In general, the distillation unit consists of a topping and a refining section. The low-boiling-point components and dissolved gases are removed in the topping column. Methanol, water, and ethanol are separated in the refining section. For fuel-grade methanol, higher alcohols, hydrocarbons, and traces of acetone and aldehydes are not a limiting factor [94Uhd]. Thus, a one-column distillation covers the requirements for fuel-grade methanol (neat methanol for use in combustion engines). A broader use of methanol fuel in the future, e.g. for fuel cells, will probably impose new requirements. Figure 6.3.15 shows the schematic of a one-column distillation plant for fuel-grade methanol production [94Uhd].

#### 6.3.2.1.2 Liquid-phase methanol synthesis

Conventional methanol synthesis reactors use fixed beds of catalysts and the syngas conversion is a heterogeneous gas-phase reaction. The main part of the liquid-phase methanol synthesis process is a slurry bubble column reactor in which the catalyst is suspended in powder form in an inert mineral oil slurry. The mineral oil acts as a heat removal medium, transferring the reaction heat from the catalyst surface to a heat exchanger. Since the heat transfer coefficient on the slurry side of the heat exchanger is relatively

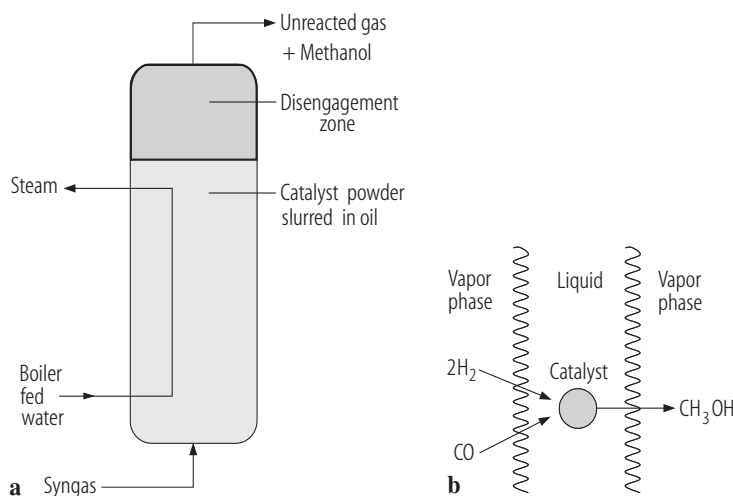
large, the heat exchanger occupies only a small part of the reactor cross-sectional area. As a result of this unique capability of efficient heat removal, a highly uniform reaction temperature throughout the entire length of the reactor can be achieved. Thus, a slurry reactor can operate with a much higher synthesis gas conversion rate per unit reactor volume than the gas-phase reactors. The LPMEOH<sup>TM</sup> (liquid-phase methanol) technology can process synthesis gases with a very high content of carbon oxides (stoichiometric factor up to 5.6). In gas-phase methanol synthesis, the temperature regulation is achieved by recycling large quantities of hydrogen-rich gas, utilizing the higher heat capacity of H<sub>2</sub> (14.4 kJ kg<sup>-1</sup> K<sup>-1</sup> at 0°C [84VDI]) compared to CO (1.05 kJ kg<sup>-1</sup> K<sup>-1</sup> at 0°C [84VDI]) for heat removal. In contrast, a liquid-phase reactor can easily cope with CO concentrations in excess of 50% without any negative effects on the catalyst activity [98All]. The slurry reactor is suitable for rapid ramping and for frequent stop/start actions. It is therefore especially suitable for integration in IGCC (integrated-gasification combined-cycle power production) facilities.

Another important feature of the LPMEOH<sup>TM</sup> process is the produced methanol quality. Due to the high CO concentration of the synthesis gas, the process leads to a raw methanol with extremely low water concentrations (ca. 1-2 wt-%), as compared to the products of gas-phase reactors with about 4-20 wt-% water. A further unique feature of the LPMEOH<sup>TM</sup> process is the ability to withdraw spent catalyst slurry and to add fresh suspension on-line. Figure 6.3.16 shows the LPMEOH<sup>TM</sup> reactor and the reaction schematics.

The process was developed during the 1980's for integration in coal gasification power plants (IGCC) to convert excess CO-rich synthesis gas into methanol. The owners of the LPMEOH<sup>TM</sup> technology are Air Products and Eastman. The first commercial-scale demonstration plant was located at the Eastman Chemical Company's coal gasification plant in Kingsport, Tennessee, USA. The plant, which produces 260 t of methanol per day, started operation in April of 1997 [98Hey].

It is estimated that the LPMEOH<sup>TM</sup> process, due to its characteristic features, is especially suitable for methanol synthesis from bio-syngas for the following reasons:

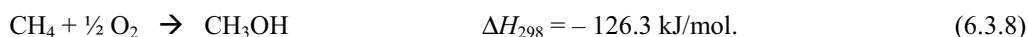
- 1) Downscaling of the process for decentralized biomass applications is more feasible than for the gas-phase process;
- 2) The biomass-derived synthesis gases are usually non-stoichiometric (high CO+CO<sub>2</sub> concentrations compared to H<sub>2</sub>) and are therefore not recommended for gas-phase synthesis without stoichiometry adjustment;
- 3) The system with dispersed catalyst in a neutral liquid reaction medium may tolerate higher impurities in the synthesis gas as compared to gas-phase catalysis;
- 4) The catalyst can be replaced during plant operation.



**Fig. 6.3.16.** (a) Schematic presentation of LPMEOH<sup>TM</sup> reactor. (b) Reactions of the LPMEOH<sup>TM</sup> process. Synthesis conditions: 50-100 bar pressure, 250°C temperature.

### 6.3.2.1.3 Direct oxidation of methane to methanol

The direct oxidation of methane into methanol is considered as a promising method for the exploitation of natural gas resources in remote areas through its conversion into methanol, an easily transportable fuel and chemical. The process allows a more direct, simple, efficient, and cheaper method for converting methane (natural gas and bio-gas) into methanol, thereby avoiding the synthesis gas path. From the thermodynamic point of view, the reaction is exothermic and favored at high pressures.



Even though many scientific groups are involved in the study of the process, there is no industrial application available at present. The partial oxidation of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  has been investigated in the homogeneous gas phase and over various catalytic materials. The results are very similar, with  $\text{CH}_3\text{OH}$  yields typically below 2% [95Loe]. Many experiments with and without catalysts were carried out at high pressures (20 to 100 bar) and high temperatures (around 400–450°C) in order to improve kinetics and methanol yield. However, the results remain modest with methanol yields of 2.5–6.5% and a methanol selectivity ranging from 20 to 50% [96Aru]. Typical oxygen concentrations used in experiments range from 2 to 10%. An increase of the oxygen concentration (aimed to increase the methanol yield) leads to a dramatic reduction of the methanol selectivity. In terms of renewable fuels, the direct oxidation of methane to methanol could be advantageous to exploit the methanol production potential of bio-gas resources.

### 6.3.2.1.4 Methanol synthesis from $\text{H}_2$ and $\text{CO}_2$

Renewable electricity can be stored by producing hydrogen via water electrolysis and converting the hydrogen and  $\text{CO}_2$  into methanol. Besides biomass and fossil resources,  $\text{CO}_2$  is also a carbon source for methanol synthesis.  $\text{CO}_2$  can be obtained from concentrated  $\text{CO}_2$  sources like flue gases from power stations and cement factories, but it can also be recovered from the atmosphere. In nature, the atmosphere serves as the carbon source for biomass growth by photosynthesis. The  $\text{CO}_2$  fixation process of photosynthesis can be imitated in a technical process, powered by renewable energy and with higher energetic efficiency (artificial photosynthesis) [78Ste, 93Spe, 95Ban, 95Stu, 96Wei]. The question of which  $\text{CO}_2$  source is the better option – flue gas or air – depends on the boundary conditions.  $\text{CO}_2$  gained from flue gases is energetically more favorable compared to recovered atmospheric  $\text{CO}_2$ . However, the separation of  $\text{CO}_2$  from flue gases requires additional fossil fuel consumption, which in turn results in additional  $\text{CO}_2$  production.  $\text{CO}_2$  from the atmosphere offers the advantage of a nearly  $\text{CO}_2$ -neutral process. Chemical, electrochemical, and photo-electrochemical methods have been used to find out which is the most efficient method of  $\text{CO}_2$  fixation. Among all of these methods, only the heterogeneous gas-phase catalytic conversion of  $\text{CO}_2$  with hydrogen can be technically realized today.

A bench-scale test plant for the heterogeneous catalytic synthesis of methanol from electrolytically generated hydrogen and  $\text{CO}_2$  was operated at the Center for Solar Energy and Hydrogen Research (ZSW), Germany [98Spe2]. The process was designed for methanol generation from atmospheric  $\text{CO}_2$ . Due to the low concentration of  $\text{CO}_2$  in the air (ca. 0.037 vol-%), the recovery of larger quantities of  $\text{CO}_2$  from the air requires new, highly efficient technologies with low specific energy consumption. Figure 6.3.17 shows the technical realization for  $\text{CO}_2$  recovery from the atmosphere. During the  $\text{CO}_2$  absorption process from the air,  $\text{K}_2\text{CO}_3$  is formed from a  $\text{KOH}$  solution in a scrubbing column. The recovery of  $\text{CO}_2$  from the carbonate solution produced in the absorption column occurs by acidifying the spent absorption solution ( $\text{K}_2\text{CO}_3$ ) with sulphuric acid in a stripper column. Besides  $\text{CO}_2$ , a  $\text{K}_2\text{SO}_4$  solution is formed in the neutralization process. An electrodialytic process with bipolar membranes is used for the regeneration of the caustic scrubbing liquid and the acidic solution from the  $\text{K}_2\text{SO}_4$  solution. Electricity (renewable) and air are input into the system, and the resulting output is pure  $\text{CO}_2$  and  $\text{CO}_2$ -lean air. The process is operated in a closed loop without any further material demand or waste streams.

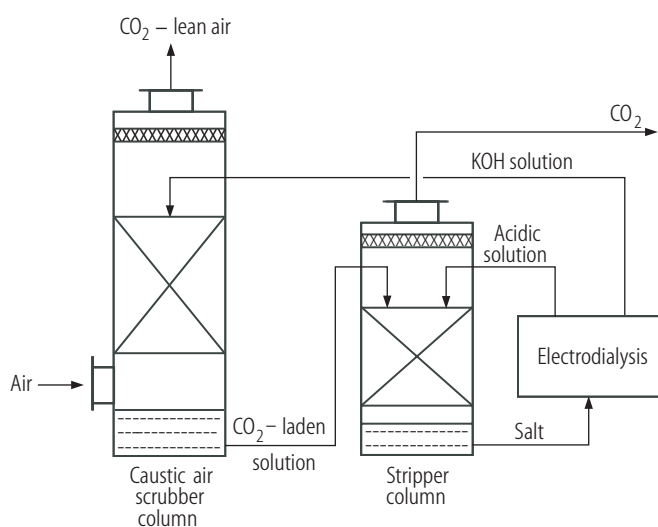
Methanol is produced by a heterogenic catalytic conversion of a gas mixture containing 25 Mol%  $\text{CO}_2$  and 75 Mol% (electrolytically generated) hydrogen over a modified  $\text{Cu/ZnO}$ -catalyst according to equation (6.3.7). In the bench-scale methanol reactor, high space-time yields of  $0.7 \text{ kg}_{\text{MeOH}} \text{ l}_{\text{catalyst}}^{-1} \text{ h}^{-1}$  could be

achieved for reaction conditions of 260°C, 80 bar, at a technically relevant space velocity of 8000  $\text{l}_{\text{syngas}} \text{l}_{\text{catalyst}}^{-1} \text{h}^{-1}$ . A total carbon conversion of 98% is estimated with the recycling of the non-reacted synthesis gas.

Alternative concepts with a membrane separation process for  $\text{CO}_2$  recovery from the atmosphere instead of an absorber column and a combined electrolysis/electrodialysis process of  $\text{K}_2\text{CO}_3$  to produce  $\text{H}_2/\text{CO}_2$  (and  $\text{O}_2$ ) in parallel were proposed by [95Stu].

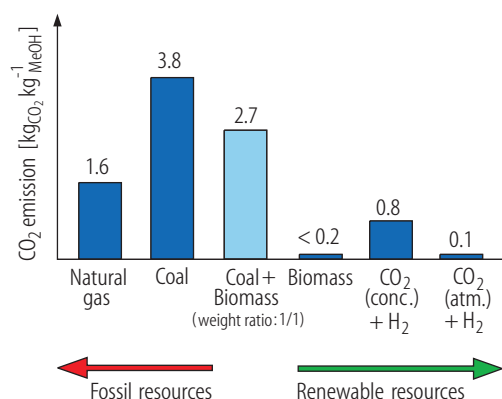
Since renewable methanol from  $\text{CO}_2$  requires hydrogen derived from renewable energy, production sites would generally be located in remote areas where these energy sources are abundant but far away from the energy demand site (e.g. hydropower). A process for the recovery of  $\text{CO}_2$  from the atmosphere can be located at the methanol production site, whereas the  $\text{CO}_2$  from concentrated emissions has to be transported from the recovery to the fuel production site. The “concentrated  $\text{CO}_2$  path” is more energy efficient than the “atmospheric  $\text{CO}_2$  path”, but the latter offers the advantages of avoiding long-distance  $\text{CO}_2$  transportation and the additional  $\text{CO}_2$  production caused by the recovery process itself. If atmospheric  $\text{CO}_2$  and renewable energy are used for the fuel production, this energy system is almost climate neutral.  $\text{CO}_2$  emission calculations are presented in Fig. 6.3.18 for the comparison of methanol production from different feedstock, including  $\text{CO}_2$  from flue gas, from air, and renewable electricity.

The implementation of the concept outlined above for the production of methanol only makes sense at places where surplus renewable electricity is available - e.g. hydropower in Iceland, Greenland, and other non-grid-connected remote areas or at future solar farms in the sunbelts of the earth. Taking into account the entire production chain from  $\text{CO}_2$  recovery from flue gases up to methanol, an overall energy efficiency of 46% (LHV of methanol with regard to overall energy demand) was calculated [98Spe1]. This value is subject to improvements of up to 50% if advanced  $\text{CO}_2$  recovery technologies are considered, e.g.  $\text{CO}_2$  recovery in fossil-fuel-powered plants before combustion. If atmospheric  $\text{CO}_2$  is taken as the carbon source for methanol synthesis, the production should be localized where the regenerative primary energy is available so that no  $\text{CO}_2$  transportation is required. The concept with atmospheric  $\text{CO}_2$  has considerable advantages over the  $\text{CO}_2$  recovery from flue gases with regard to the overall  $\text{CO}_2$  emissions for methanol production and utilization. However the energy efficiency of 38-46% is lower, mainly due to the low  $\text{CO}_2$  concentration in the atmosphere (ca. 0.037 vol-%) compared to flue gas  $\text{CO}_2$  concentrations of up to 15 vol-% [98Spe1, 98Spe2]. Methanol production via  $\text{CO}_2/\text{H}_2$  is an energy storage method which can be used without a greenhouse effect. It is a convenient fuel and also a raw material for hydrocarbon fuels via e.g. the Methanol-To-Gasoline (MTG) or the Methanol-To-Olefins (MTO) route.



**Fig. 6.3.17.** Process design for  $\text{CO}_2$  recovery from the atmosphere.





**Fig. 6.3.18.** CO<sub>2</sub> emissions for methanol utilization and production from fossil raw materials (via steam reforming/gasification), from biomass (via gasification), from flue gas CO<sub>2</sub> (conc.) and renewable electricity, and from atmospheric CO<sub>2</sub> and renewable electricity [99Spe1].

### 6.3.2.2 Fischer-Tropsch synthesis of gasoline and diesel fuels

Liquid synthetic hydrocarbon fuels, such as synthetic gasoline or diesel, can be produced via synthesis gas from either fossil or renewable resources. They can be used within the existing infrastructure for liquid fuels, but possess considerable advantages compared to conventional fuels. They are free of sulphur and have a very low aromatics content, therefore substantially reducing the environmentally harmful emissions like volatile hydrocarbons, aromatics, SO<sub>2</sub>, particulates, etc. The automobile and mineral oil industry consider synthetic diesel fuel from natural gas as a promising fuel for the medium-term future (10-20 years). In a long-term perspective (> 50 years), the renewable resources may take the major share.

The Fischer-Tropsch (FT) conversion of synthesis gas into hydrocarbons was discovered in Germany in the 1920's. The key step is the conversion of synthesis gas into waxy hydrocarbons. A simplified representation is:

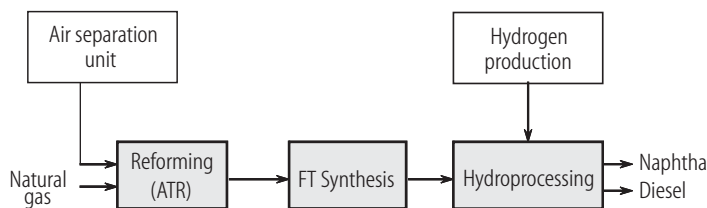


The desired products of a Fischer-Tropsch diesel fuel are C<sub>10</sub> - C<sub>23</sub> hydrocarbons. The selectivity of a carbon number product cut is a function of the probability of chain growth, which can be influenced by the type of catalyst (cobalt- or iron-based) and the synthesis conditions like temperature, pressure, and syngas composition. Nevertheless, only a fraction of the product can be directly used as diesel fuel. The rest must be upgraded to fuel quality. Therefore, the (waxy) Fischer-Tropsch product is treated in a downstream hydro-cracking/hydro-isomerization process to form middle-distillate products.

Cobalt-based catalysis dominated the industrial application of FT synthesis over a period of 25 years (1925-1950) until the iron catalysts became established. However, due to its higher activity and stability, the cobalt-based catalysts experienced a renaissance in the last decade, e.g. in the SASOL SPD (slurry-phase distillate) process for middle-distillate fuels [02SAS]. Many types of reactors have been tested over the 60 years since the process discovery. At present, the slurry-phase reactors seem to offer more advantages than the classic tubular fix-bed reactors. Some of these advantages, regardless of whether a cobalt or an iron catalyst is employed, are:

- The reaction phase is well-mixed, assuring isothermal conditions and excellent temperature control;
- Large-scale tubular reactors operate with much higher pressure drops and lower space charge than slurry reactors;
- On-line catalyst removal;
- Cost-effective construction, operation, and maintenance;
- Easy up-scaling possibilities; it is estimated that tubular fix-bed reactors can reach a potential capacity of 3000 to 4500 barrel/day, whereas a single slurry-bed reactor can process ca. 20000 barrel/day [95Jag, 98Jag].





**Fig. 6.3.19.** The slurry-phase distillate (SPD) process steps [02SAS].

In the following, a short, exemplary description of the SASOL slurry-phase distillate process is given. The Fischer-Tropsch reaction has been used by SASOL since 1955 for producing liquid fuels and chemicals from synthesis gas to overcome the South Africa oil import restrictions. Besides several generations of SASOL fluidized-bed processes (e.g. Synthol process practiced by SASOL and Mossagas Ltd. in South Africa), the slurry processes were developed at SASOL. Today's modern SASOL technology is based on SPD technology. The slurry-phase distillate process converts syngas into high-quality diesel as the main product. Slurry reactors typically operate at temperatures around 220–240°C and 20–25 bar pressure.

The whole SASOL slurry phase distillate process consists of three main process steps (Fig. 6.3.19). After syngas generation, the gas is fed into the bottom of the reactor (see Sect. 6.3.2.1.2) where it is distributed into the slurry phase consisting of an inert solvent (waxy hydrocarbons) and catalyst particles. The synthesis gas diffuses into the liquid-solid mixture and is converted into hydrocarbon products by the FT reaction. The heat generated in the reaction is easily transported by the liquid reaction medium and removed through the reactor cooling coils while generating steam. The product is then separated from the slurry containing the catalyst particles and the volatile compounds and water leave the reactor at the top. The third step is the upgrading unit, where hydro-cracking and hydro-isomerization processes produce middle-distillate products such as diesel, kerosene, and naphtha (naphtha 20% and middle distillate 80%). The thermal efficiency of the process is calculated to be about 60% with regard to natural gas as feed-stock based on the lower heating value and the overall carbon efficiency is about 75% [02SAS].

Other technology developments, e.g. the Shell process, are based on conventional fixed-bed reactors. The Shell Middle-Distillate Synthesis (SMDS) process is successfully applied in Bintulu, Malaysia, to produce a synthetic diesel fuel from natural gas on a scale of 12500 barrels/day [99Hey].

Large amounts of low-cost natural gas are available in remote areas that do not have any infrastructure for transport. Many companies are seeking opportunities for developing technologies to use methane resources for synfuel production via Fischer-Tropsch technology, especially for monetizing the crude-oil-associated gas as an alternative to flaring. The key for the economic viability of the FT process is the cost of natural gas today, the future development of the crude oil price, and the accessibility of a suitable product market. In the far future, FT fuels might also be an energy vector for biogeneous feedstock.

#### 6.3.2.2.1 Fischer-Tropsch synthesis from CO<sub>2</sub> and H<sub>2</sub>

The FT synthesis can also be conducted with CO<sub>2</sub> and H<sub>2</sub> instead of conventional synthesis gas. However, there is presently no technical application for this process. Along with renewable methanol, liquid FT fuels through hydrogenation of CO<sub>2</sub> could in principle be CO<sub>2</sub> neutral, provided that the hydrogen is produced on a non-CO<sub>2</sub>-release basis. The FT hydrocarbons gained in this way would have advantages over other fuel options like e.g. renewable methanol, including an existing infrastructure and an established vehicle propulsion technique. CO<sub>2</sub> is available from fossil-fuel-powered plants or from the atmosphere. Thermodynamic considerations indicate no equilibrium constraints for the hydrogenation of CO<sub>2</sub> to hydrocarbons either in a direct reaction or through the retro-shift reaction:



H<sub>2</sub>O itself and CO<sub>2</sub> can affect the catalyst activity, with different effects for iron and cobalt catalysts. H<sub>2</sub>O strongly inhibits the iron catalyst activity and therefore reduces the possibility to achieve high reaction conversion rates [94Sch, 90Zim]. Both H<sub>2</sub>O and CO<sub>2</sub> act as oxidizing compounds in the reacting mixture and may cause oxidation and structural changes of the iron catalyst. The situation is different for cobalt catalysts. H<sub>2</sub>O action is positive in regard to hydrocarbon formation, as it suppresses the methane formation [94Sch, 97Sch], allowing high degree-of-conversion rates. CO<sub>2</sub> in a cobalt-catalyzed system only plays a diluting role, as it is either strongly adsorbed or hydrogenated. Cobalt catalysts mixed with CO-shift catalysts may also be candidates for FT CO<sub>2</sub> conversion. However, experimental investigations revealed that such hybrid catalysts can not efficiently convert CO<sub>2</sub>, as the CO partial pressure remains too low due to equilibrium constraints of the CO shift reaction. As a consequence, FT CO<sub>2</sub> hydrogenation would be possible on the industrial scale with iron catalysts, but not with cobalt. For hydrocarbon production from H<sub>2</sub>/CO<sub>2</sub>-syngas, the iron catalyst is favorable due to its CO<sub>2</sub>/CO shift conversion activity and an increase of temperature (> 300°C) is needed due to the higher CO equilibrium concentration. Alkalized iron on γ-alumina demonstrated the best conversion rates in a FT conversion of CO<sub>2</sub> [99Rie].

### 6.3.3 Bio-fuels via fermentation

#### 6.3.3.1 Ethanol production technologies

Ethanol is produced by the fermentation of sugar according to the chemical reaction



Only a few plants contain sugar, e.g. sugar cane, sugar beet, and fruits. Larger carbohydrate molecules such as starch (e.g. in potatoes and grains) or cellulose (e.g. in wood and straw) must be first broken down to sugar (glucose) prior to undergoing fermentation. A schematic presentation of the production routes, various resources, and by-products in ethanol production is shown in Fig. 6.3.20.

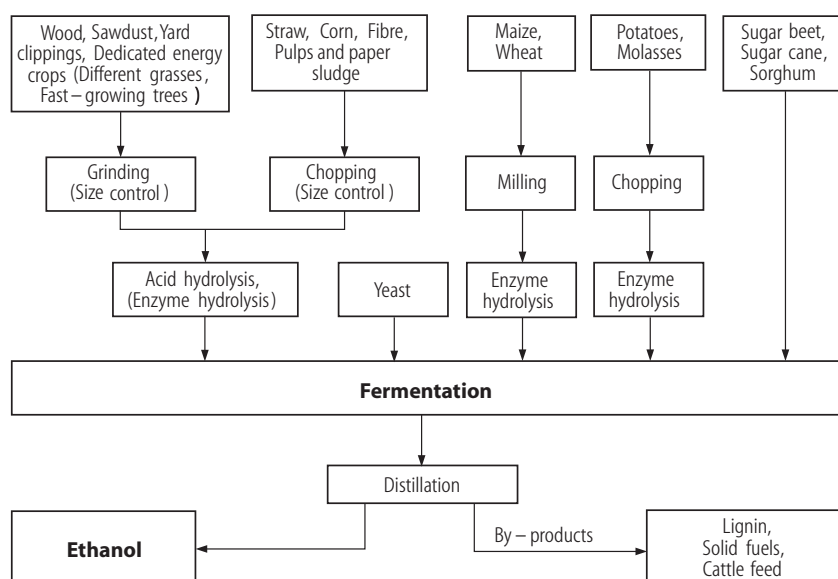


Fig. 6.3.20. Ethanol production routes from various biomass sources.

**Table 6.3.5.** Average ethanol yields from different crops.

Crop	Ethanol yield [l ha <sup>-1</sup> a <sup>-1</sup> ]
Sugar cane	5150
Sugar beet	4755
Sorghum	3680
Sweet sorghum	2800
Corn grain	2800
Wheat	2080

The technology for ethanol production from cellulose materials is not yet state-of-the-art. An efficient enzymatic hydrolysis of cellulose is not yet commercially available. Applying acid hydrolysis to cellulose materials is expensive and reduces the yield of sugar. The deployment of new enzymes, however, may allow the economic production of ethanol from cellulose in the future. A range of cellulose-containing biomass feedstock, including straw, corn fiber, sawdust, pulp and paper sludge, and dedicated energy crops (e.g. different grasses and fast-growing trees) are available for ethanol production once enzymatic hydrolysis is successful.

As shown in Fig. 6.3.20, the differences between the routes of ethanol production from various raw materials mostly concern the preparation of the materials and the severity of the processes which lead to a fermentable sugar form:

- 1) Sugar-containing raw materials can directly undergo fermentation;
- 2) Grains need a simple milling;
- 3) Potatoes need a size-uncritical chopping;
- 4) Wood and cellulose materials require costly cutting-up processes and strict size control in order to provide an efficient subsequent hydrolysis.

The most important differences in the hydrolysis of the raw materials into fermentable sugars are in the breakdown of the polymer molecules. Starch-containing feedstock needs a simple enzymatic hydrolysis, whereas cellulose materials need mostly an acid hydrolysis. Great efforts are in progress towards the commercialization of cellulose-to-ethanol technology [96Ela]. New enzymes which allow an efficient cellulose hydrolysis are being developed [02RFA].

Once fermentable sugar is obtained, the fermentation and distillation steps are basically the same for each process. The resulting ethanol is diluted in water. Concentrated ethanol is produced through distillation. The ethanol yield depends on the raw material and the technology used. Table 6.3.5 shows the average values for ethanol yield from different crops [96Ela].

### 6.3.3.2 Bio-gas production via anaerobic digestion

Anaerobic digestion is a biological process that produces a gas principally composed of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), also known as bio-gas. Bio-gas is produced from organic wastes such as live-stock manure, food processing waste, etc. Organic waste and various types of bacteria are put in an air-tight container called a digester where the process occurs. Depending on the waste feedstock and the system design, bio-gas typically contains 55-75 vol-% CH<sub>4</sub> and 25-45 vol-% CO<sub>2</sub>.

Many anaerobic digestion technologies are commercially available and have been demonstrated for use with agricultural wastes and for treating municipal and industrial wastewater. Process temperature affects the rate of digestion and should be maintained in the mesophilic range (35-40°C) with an optimum of 38°C. It is also possible to operate in the thermophilic range (57-63°C), but this digestion process is subject to upset if not closely monitored.

The attainable maximum gas yield as well as the  $\text{CH}_4$  content (55-75 vol-%) essentially depends on the type of substrate, temperature, processing, retention time in the digester, pH value, and substrate supply. Along with the main gas components  $\text{CH}_4$  and  $\text{CO}_2$ , the bio-gas contains small concentrations of  $\text{H}_2\text{S}$  (0-1 vol-%),  $\text{H}_2$  (0-1 vol-%),  $\text{CO}$  (0-1 vol-%),  $\text{N}_2$  (0-3 vol-%),  $\text{O}_2$  (0-2 vol-%), and traces of  $\text{NH}_3$ .

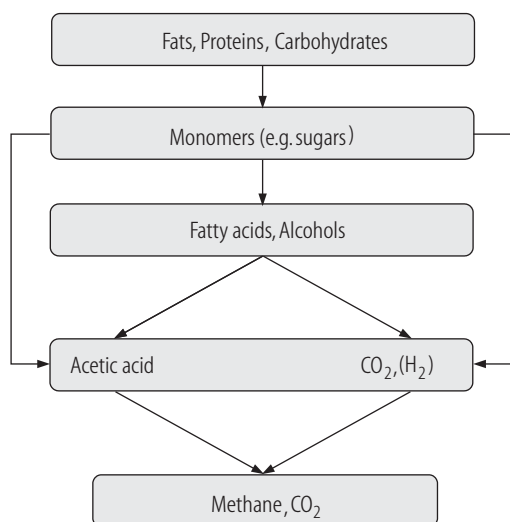
A schematic representation of the digestion process via the different intermediate products occurring during anaerobic digestion is presented in Fig. 6.3.21. The process of anaerobic digestion consists of several steps:

- The first step is the decomposition (hydrolysis) of plant or animal matter. This step breaks down the organic material to usable-sized monomers such as sugar.
- The second step is the conversion of decomposed matter to organic acids and alcohols.
- In a third step, organic acids and alcohols are converted into acetic acid, hydrogen, and  $\text{CO}_2$ .
- In a last process step, acetic acid is decomposed into methane and carbon dioxide.

Different micro-organisms are involved in each process step. The anaerobic fermentation processes differ according to the processing (1- or 2-step processing) and according to the solid content (wet and dry fermentation). In two-stage systems, the hydrolysis and the acidification run separately from the methane formation process. The wet process requires a mixture with ca. 90 wt-% water. The dry procedures operate with about 60-70 wt-% water.

The bio-gas digester size generally ranges from  $150 \text{ Nm}^3$  to about  $500\text{-}1000 \text{ Nm}^3$  in volume. A bio-gas reactor with a volume of  $1000 \text{ Nm}^3$  can process ca. 11000 t of biomass per year. The bio-gas yield of a  $1000 \text{ Nm}^3$  digester, depending on the feed (manure, fats, grass), ranges from 200000 to 700000  $\text{Nm}^3$  per year. The biomass residence time in the digester is usually 25 to 35 days, longer for dry fermentation. The fermentable biomass feed is generally characterized by its organic matter (OM) content. In Table 6.3.6, the maximum attainable bio-gas yields of different biomass are listed based on the organic matter content.

The use of organic waste for bio-gas production is a state-of-the-art technology and is operating in many farming units. At nearly all of the plants, the produced bio-gas is converted to electricity, but it can also be used as a substitute natural gas (SNG) for other applications. After removing  $\text{CO}_2$  and major impurities from bio-gas, it can be used directly as transport fuel or can be fed into the existing natural gas distribution network and used as a gaseous fuel along with natural gas. Scrubbing processes or the pressure swing adsorption (PSA) technique can be applied to separate  $\text{CO}_2$ .



**Table 6.3.6.** Maximum attainable bio-gas yield of different substrates.

Biomass	Bio-gas yield [ $\text{Nm}^3 / \text{kg}_{\text{org. matter}}$ ]
Animal fats	1.00
Animal manure	0.30
Grass	0.70
Food wastes	0.50
Corn	0.90
Beets	0.95

**Fig. 6.3.21.** Intermediate products occurring during anaerobic digestion [95Kuh].

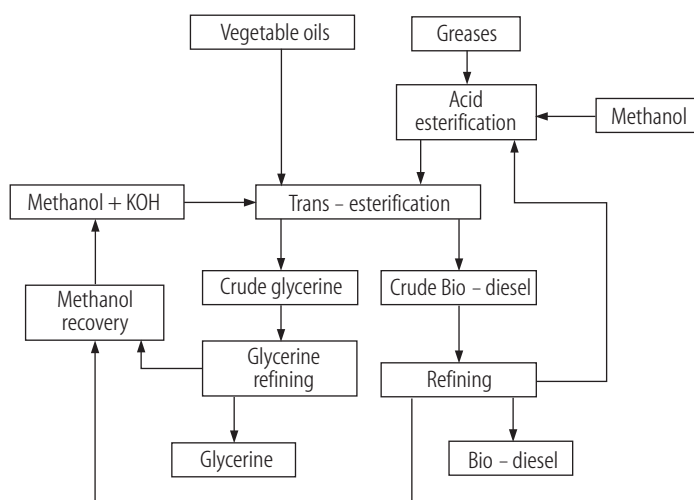
### 6.3.4 Bio-fuels from oil plants

Vegetable oils gained from different seeds can be considered as potential transportation fuels and can substitute fuel oils in stationary applications. However, the application of neat plant oil is restricted to the use in specially adapted internal combustion engines. This fuel is not standardized yet and a large-scale market penetration as transportation fuel is still doubtful. Only the esterified forms of the plant oils are suitable for a larger scale application.

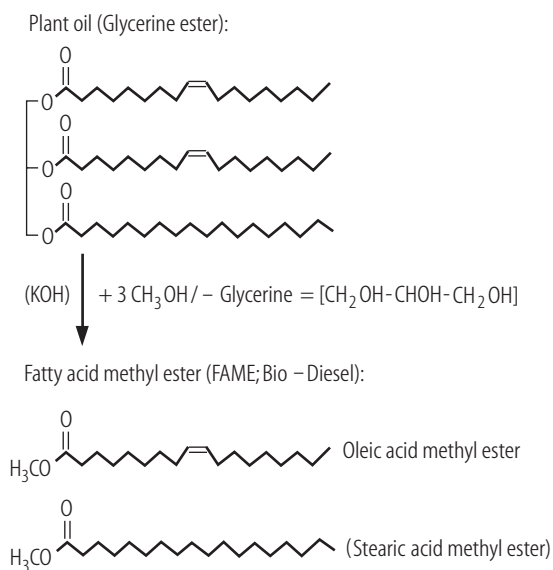
Through trans-esterification the oils are chemically transformed into a diesel-like fuel called bio-diesel. Bio-diesel is a name given to all fatty esters when they are used as fuel. Just like petroleum diesel, bio-diesel can fuel compression-ignition engines. Bio-diesel, a fatty acid methyl ester (FAME) can be produced from many natural fatty materials such as plant oils, animal fats, recycled cooking greases, etc. A widely used form of bio-diesel, especially in Europe, is the rapeseed methyl ester (RME). Other vegetable oils which can be esterified with methanol to produce bio-diesel are soybean oil, palm oil, etc. Figure 6.3.22 schematically presents the basic technology for bio-diesel production.

Vegetable oils, gained by pressing and extraction, or fats (greases) undergo an alkaline or acidic hydrolysis and trans-esterification with methanol. In this process, the original fatty acid ester with glycerine is split into fatty acid and glycerine (see Fig. 6.3.23). The fatty acid reacts with the methanol added to the solution yielding bio-diesel. The hooked tripod molecule is transformed into slippery ester chains, thus reducing the viscosity to that of a diesel-like fuel. Due to the equilibrium conditions, the reaction stops at a transformation grade of the oil of ca. 2/3. In order to enhance the trans-esterification reaction, the glycerine is gradually removed from the system. The crude bio-diesel and the crude glycerine undergo a refining step in order to recover the unreacted products, e.g. methanol, which are reintroduced to the process. An average yield of  $3.5 \text{ t ha}^{-1} \cdot \text{a}^{-1}$  rapeseed produces  $1.33 \text{ t ha}^{-1} \cdot \text{a}^{-1}$  of rapeseed oil, from which, after trans-esterification with  $0.14 \text{ t}$  methanol,  $1.32 \text{ t}$  of bio-diesel can be gained [95Sch].

The main distribution of bio-diesel in Europe is for utilization as a neat fuel or blended into conventional diesel fuel. Blends of up to 5 vol-% (B5) bio-diesel with diesel fuel can be used in all diesel systems and are compatible with the existing transport, storage, and distribution equipment. This low-level blend does not require any engine or infrastructure modification. Pure bio-diesel (B100) can be used in many engines built since the mid-nineties with minor modifications. Earlier-model cars may have rubber seals in the fuel system which can fail if B100 is used. Nevertheless, the distribution of bio-diesel as B100 will be problematic in the future due to exhaust gas limitations with alternative diesel/bio-diesel operation. Therefore, most bio-diesel will be sold as a blend in the future.



**Fig. 6.3.22.** Basic technology for bio-diesel production.



**Fig. 6.3.23.** Production of FAME via transesterification. The glycerine ester is converted to the methyl ester with MeOH. The main compound in rapeseed plant oil methyl ester (RME) is oleic acid glycerine ester (CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub>-CH=CH-(CH<sub>2</sub>)<sub>7</sub>-CO-O-CH<sub>3</sub>), but other fatty acid methyl esters are also present in FAME.

### 6.3.5 Bio-pyrolysis oil

Fast (or flash) pyrolysis is a high-temperature process in which biomass is heated rapidly (< 2 seconds) up to ca. 500°C in the absence of oxygen. Under these reaction conditions, the biomass decomposes by generating gases, vapors, aerosols, and charcoal. The condensed vapors form the bio-pyrolysis oil. The essential features of the fast pyrolysis process are:

- Very high heat-transfer rates, which usually require a finely ground biomass feed;
- The carefully controlled pyrolysis temperature of about 500°C;
- The biomass and vapor residence time is very short, typically less than 2 seconds;
- The pyrolysis vapors are rapidly cooled down to obtain the pyrolysis liquid and to avoid gas-phase reactions which are detrimental for the oil quality.

Bio-pyrolysis oil is a complex mixture of water and organic compounds with the main chemical components listed in Table 6.3.7. It is chemically unstable and undergoes several inter-component chemical reactions leading to larger molecules. The main chemical reactions which take place are polymerization of double-bonded compounds, as well as etherification and esterification between hydroxyl, carbonyl, and carboxyl group compounds. The instability of the liquids increases with increasing temperature. This trait should be taken into consideration when planning their storage, transport and use. The viscosity is also sensitive to temperature and storage time due to an increasing average molecular weight over time [97Oas, 96Bri, 99Bri2].

The bio-pyrolysis oil can potentially substitute fuel oil or diesel in stationary applications including boilers, furnaces, engines, and turbines for heat and electricity generation, respectively. Upgrading bio-pyrolysis oil to transportation fuels by hydrogenation is feasible but currently not economic due to the large hydrogen demand.

A wide range of reactor configurations have been developed for bio-pyrolysis oil production. However, fluid beds are the most popular due to their ease of operation and upscaling. A concept for a fluid bed fast pyrolysis process is presented in Fig. 6.3.24 [99Bri1]. In order to minimize the water content in the fast pyrolysis product and to avoid difficulties with grinding (around 2 mm) and feed, the biomass should be dried to a water content less than 10 wt-%.

A relatively new reactor configuration is the rotating cone reactor, invented at the University of Twente and being developed by the Biomass Technology Group (BTG) [97PYN]. This reactor operates

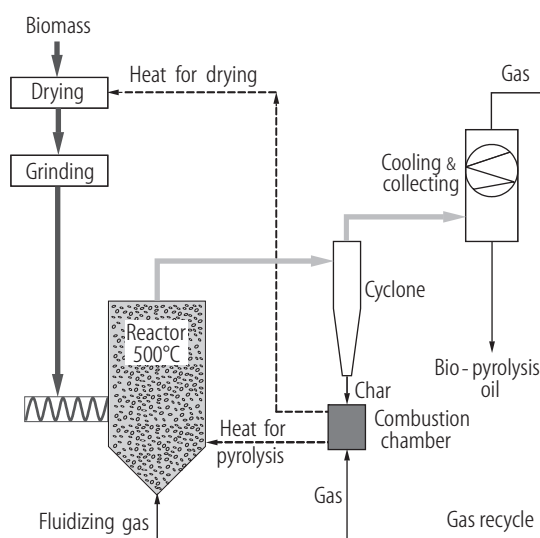
as a transported-bed reactor. However, the transport is carried out by centrifugal forces and not by gases. Biomass particles and hot sand are fed to the bottom of a rotating cone and transported upwards by the rotating action of the cone. The short gas-phase residence time and high heating rate achieved with this system lead to a high bio-pyrolysis oil yield (up to 80 wt-%).

The utilization of bio-pyrolysis oil as an intermediate energy carrier is widely discussed, because it offers the possibility of decentralized processing of biomass with a centralized conversion of the bio-pyrolysis oil to produce synfuels via the syngas route (e.g. in refineries). Whereas long-distance transport is not favorable for untreated biomass, bio-pyrolysis oil can be economically transported due to its higher volumetric energy density. In addition to bio-pyrolysis oil, charcoal or charcoal/bio-pyrolysis oil slurries can also be used as intermediates to separate biomass processing and fuel synthesis [02Hen].

In principle, the bio-pyrolysis oil can be converted *in situ* by catalytic hydro-treating of the hot pyrolysis gas or *ex situ* after obtaining the liquid bio-pyrolysis oil. Reaction conditions for the catalytic hydrogenation are 250-400°C and 20-200 bar with Co/Mo or Ni/Mo catalysts based on  $\text{Al}_2\text{O}_3$  as support. The main problem is the high oxygen content in bio-pyrolysis oil, requiring high amounts of hydrogen for the conversion process. Another problem is carbon formation from the bio-pyrolysis oil at the catalysts. Therefore, it is doubtful that these processes will play a relevant role in the future.

**Table 6.3.7.** Typical composition of bio-pyrolysis oil produced from wood.

Main Components		wt-%
Water	$\text{H}_2\text{O}$	< 40
Hydroxy acetaldehyde	$\text{HOCH}_2\text{COH}$	$\approx 15$
Acetol	$\text{HOCH}_2\text{COCH}_3$	$\approx 10$
Formic acid	$\text{HCOOH}$	$\approx 3$
Acetic acid	$\text{H}_3\text{C COOH}$	$\approx 5$
Levoglucosan	$\text{C}_6\text{H}_{10}\text{O}_5$	$\approx 7$



**Fig. 6.3.24.** Conceptual fast pyrolysis process with fluidized bed [99Bri1].



### 6.3.6 Further fuel production paths

#### 6.3.6.1 Hydrogen

Although hydrogen production is described in detail in [Chap. 7](#), a short digression on the subject is presented here. Hydrogen has the major advantage that it is accessible via several production paths. The electrolytical processes are the technical state-of-the-art – even for fluctuating operation with renewable electricity.

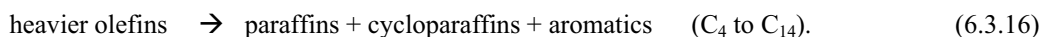
For hydrogen production from biomass, it is necessary to distinguish between the thermo-chemical and the biological conversion techniques. In the thermo-chemical method, the biomass is heated and converted into a gas in the presence of a gasification agent like air, oxygen, or water vapor. The resulting gas is then conditioned and cleaned in a subsequent step. The CO content in the synthesis gas is converted to hydrogen and CO<sub>2</sub> by using water vapor in the water-gas shift reaction. Finally, the hydrogen is separated from the residual gas (CO<sub>2</sub>, remaining CO, water vapor, N<sub>2</sub>) by pressure swing adsorption (PSA).

In contrast to the thermo-chemical conversion techniques, the biological methods operate in a temperature range well below 100°C. A methane-containing bio-gas is first produced during anaerobic fermentation, which can then be converted to hydrogen through steam reforming. Ethanol attained from sugar- or starch-containing plants using fermentation methods can also be converted to hydrogen by reforming. The direct fermentation to a hydrogen-containing gas through the use of suitable bacteria cultures is not state-of-the-art at this time. The photo-biological methods, which directly produce hydrogen under exposure to light, are also not yet mature.

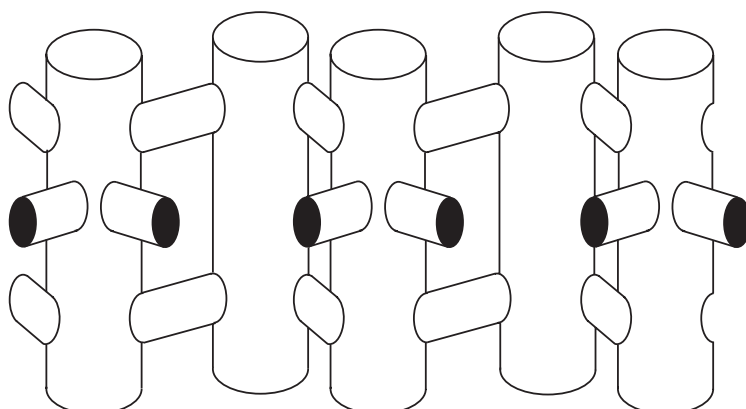
Further production methods include thermo-chemical cycle processes in which, for example, metal oxides are reduced upon exposure to concentrated solar irradiation and afterwards release hydrogen through a steam treatment. Another future option is photo-electrochemistry, where hydrogen is released at a semiconductor/electrolyte interface through direct exposure to solar radiation.

#### 6.3.6.2 Methanol-to-gasoline (MTG) process

The Methanol-To-Gasoline (MTG) process was discovered in 1976 [\[83Cha\]](#) and then rapidly developed into an industrial process by Mobil Company. A 14000-barrel-per-day plant was built in New Zealand in the early 1980s. The MTG process produces gasoline which is higher in octane than gasoline produced from oil. The reaction mechanism is not completely understood, but the generally accepted reaction pathway is [\[84Mey\]](#):



The process temperatures are around 350–450°C at pressures from one to several bars. The process uses a selective zeolite catalyst and is very exothermic. During the early stages of the reaction, methanol is converted to dimethyl ether and water. The initial hydrocarbons are rich in lighter olefins, and as the reaction time is increased, higher olefins and aromatic hydrocarbons are formed. Each 100 kg of methanol produces ca. 58 kg of water and 42 kg of hydrocarbons. The yield of by-products such as CO, CO<sub>2</sub>, and H<sub>2</sub> is very low, typically less than 0.5 wt-% [\[83Cha\]](#). The final composition formed over the zeolite catalyst is 60% saturated hydrocarbons, 10% olefins, and 30% aromatics [\[84Mey\]](#). The MTG process produces gasoline comparable to high-quality gasoline derived from crude oil without the need for expensive post-processing or engine modifications for use.



**Fig. 6.3.25.** Schematic presentation of the pore structure of ZSM-5.

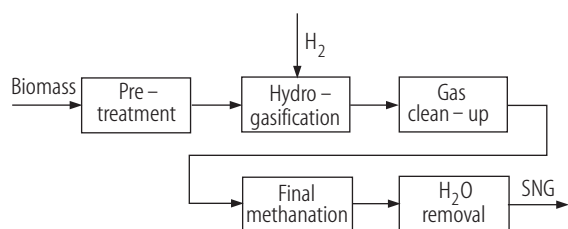
The heart of the MTG process is the zeolite ZSM-5, one of the most versatile catalysts. ZSM-5 is mainly used for hydrocarbon inter-conversions and has a high silica-to-alumina ratio. The substitution of an aluminum ion (charge 3+) for a silicon ion (charge 4+) requires the additional presence of a proton. This additional proton gives the zeolite a high level of acidity, which is responsible for its activity. ZSM-5 is a highly porous material and has an intersecting two-dimensional pore structure. It has two types of pores, both formed by 10-membered oxygen rings. The first type of pores is straight and elliptical in cross-section. The second type intersects the straight pores at right angles in a zigzag pattern and has a circular in cross-section (Fig 6.3.25). This unique two-dimensional pore structure allows a molecule to move from one point in the catalyst to anywhere else in the particle. The large openings are the elliptical, straight pores in ZSM-5. The pores created by these 10-oxygen rings are essential for the formation of the desirable components in gasoline. An 8-oxygen ring zeolite will not produce molecules with 6 or more carbons; molecules of this size will not fit into the small pores of these zeolites. On the other hand, the large pores of a 12-oxygen ring zeolite produce large amounts of C-11 and C-12 compounds, i.e. undesirable products for gasoline.

### 6.3.6.3 Synthetic (substitute) natural gas

The production of synthetic (substitute) natural gas (SNG) is an attractive alternative to hydrogen. The production of SNG is also a promising option for exploiting biomass resources. It may easily substitute natural gas and can be interchanged with pipeline-quality natural gas. The hydro-gasification (hydrogen as gasification agent) of biomass has been identified as an efficient way for converting biomass and hydrogen into SNG.

A simplified flow sheet for SNG production from biomass with hydro-gasification is represented in Fig. 6.3.26. Hydrogen and pre-treated biomass (dried and ground) are fed into a gasifier reactor (ca. 800°C, 30 bar). The product gases are routed through a high-pressure clean-up section for contaminant removal (solids, H<sub>2</sub>S, HCl, etc.). They then pass a final methanation to convert CO and H<sub>2</sub> into methane (ca. 400°C). The estimated product gas composition is: ca. 80 vol-% CH<sub>4</sub>, ca. 10 vol-% H<sub>2</sub>, ca. 10 vol-% CO<sub>2</sub>, and ca. 1 vol-% N<sub>2</sub>. The SNG production efficiency, defined as the ratio of the LHV of SNG leaving the reactor and the LHV of H<sub>2</sub> and biomass, is calculated as 81% [02ECN].

Another possible method for SNG production is the steam gasification of biomass to synthesis gas, followed by methanation. However, while steam gasification is a highly endothermic process, methanation is a strongly exothermic process. Thus, the process efficiency is lower compared to one-step hydro-gasification, a slightly exothermic process. Furthermore, steam gasification is operated at a high temperature level, and the released methanation heat is at a lower temperature level which can not be used in gasification.



**Fig. 6.3.26.** Schematic flow sheet for SNG production from biomass [02ECN].

#### 6.3.6.4 Dimethyl ether (DME)

Dimethyl ether, with physical characteristics similar to liquid petroleum gas (LPG), can be produced via methanol dehydration technology (termed as the two-step or indirect method starting from syngas). This indirect path is currently state-of-the-art and consists of a conventional methanol synthesis step followed by the downstream catalytic conversion of methanol. An alternative technology is the production directly from syngas in a single-step DME synthesis with specially designed catalysts. This technology was successfully demonstrated at some pilot plants (e.g. a 30 t/d plant from Mitsubishi Gas Chemicals, Japan).

The reaction path takes place in the two steps via (6.3.6) and (6.3.7) (methanol synthesis from syngas) and (6.3.13) (methanol dehydration):



The reaction equation for the single-step DME synthesis is



In practice, three reactions occur simultaneously:



A further reaction path is via



with the same intermediate steps as above but without the shift reaction.

The highest equilibrium conversion (e.g. 90% for 260°C/50 bar) is obtained for (6.3.17) with a  $\text{H}_2/\text{CO}$  ratio of 1, which is a substantial advantage for syngas from biomass gasification. The energetic efficiency on the LHV basis is ca. 80%. As a result of the high conversion efficiency, the life-cycle  $\text{CO}_2$  emissions of DME production from natural gas and use in vehicles are similar to those from the conventional production and use of diesel fuel obtained from crude oil.

#### 6.3.6.5 Methanol-to-synfuels (MtSynfuels) process

In addition to the conventional path for the production of synthetic hydrocarbons via the Fischer-Tropsch reaction, the MtSynfuels concept, in which the synthesis gas is first converted to methanol, was developed by Lurgi. In a downstream plant methanol is dehydrated to DME, which is then transformed to olefins, and finally the olefins are oligomerized to hydrocarbon fuels. The advantage of this route is that it can accommodate the decentralized availability of biomass as the different process steps methanol synthesis, MTP (Methanol-To-Propylene) and COD (Conversion of low-molecular-weight Olefins to Distillate) are easier to downscale than FT synthesis, including the downstream conversion to automotive fuels.

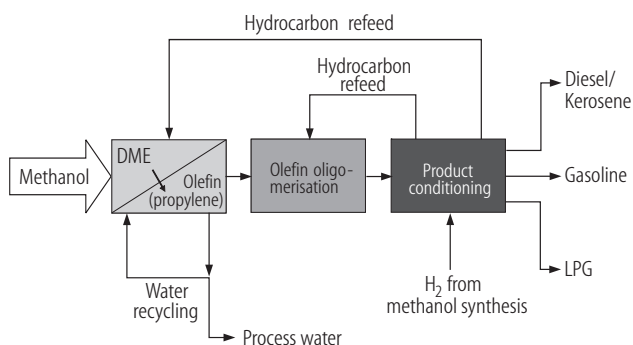


Fig. 6.3.27. The MtSynfuels concept.

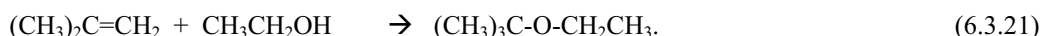
Figure 6.3.27 shows the principle of the MtSynfuels route [01Rot, 04Lie]. In a common FT plant, the synthesis gas is first converted to paraffins (long-chain hydrocarbons), which are subsequently transformed to distillates (diesel, gasoline) by hydro-cracking, a laborious and costly process. It is estimated that the MtSynfuel process has ca. 10% less investment costs and 10% higher energy efficiency as compared to the conventional FT process [04Lie]. The MtSynfuel technology is not yet commercially available. However, laboratory test results are encouraging and a market introduction in the short term seems possible.

#### 6.3.6.6 MTBE/ETBE – methyl (ethyl) tertiary butyl ether

Oxygenates are oxygen-rich compounds which, when added to gasoline fuels, enhance the octane rating and make them burn more cleanly, thereby significantly reducing toxic tailpipe pollution. Cleaner-burning oxygenated fuels are one of the leading tools in fighting automotive air pollution.

Two types of oxygenates are commonly added to gasoline: alcohols and ethers. The advantage of using ethers instead of alcohols is that no demixing of the fuel occurs at low temperatures or in the presence of water. Another advantage is that the fuel volatility decreases whereas it increases for alcohols. Methyl tertiary butyl ether (MTBE:  $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$ ) and ethyl tertiary butyl ether (ETBE:  $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2\text{CH}_3$ ) are compounds to increase the oxygen content of gasoline. MTBE is the most widely used fuel oxygenate due to its combination of technical advantages and supply availability. MTBE delivers high octane values at relatively low cost. In addition, MTBE offers low water solubility (compared to e.g. alcohols), low reactivity, and relatively low volatility. These characteristics allow refiners to overcome handling problems in the fuel distribution system posed by alcohol oxygenates. MTBE and ETBE are completely miscible with gasoline. The maximum concentrations in gasoline are 15 vol-% (according to the European regulation EN 228).

For MTBE or ETBE production, methanol or ethanol and isobutene are combined, and the etherification reaction takes place in the liquid phase at 7–10 bar and 65–95°C.

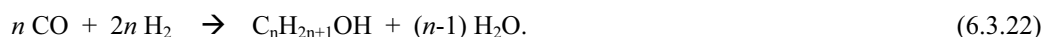


Methanol, derived primarily from natural gas, is one feedstock used in the production of the most commonly used oxygenate MTBE. Ethanol is derived primarily by fermenting agricultural products (bio-ethanol) and is used directly as an additive or as a feedstock for the production of ETBE.

Isobutene, which is the other feedstock used in the production of both MTBE and ETBE, is derived as a by-product of ethene production and from the catalytic cracking refinery process. Its availability is limited and determined by the amount of cracking. However, isobutene can also be produced by the dehydrogenation of the more abundant butanes which are contained in the by-product “wet gas” from natural gas production, as well as from refinery off-gases (dehydrogenation of isobutane,  $(\text{CH}_3)_3\text{CH}$ ) [96Wal]. For increasing the amount of isobutane, a mixed butane feed is treated in an isomerization unit before entering the dehydrogenation unit. A further production path for isobutene is from isobutanol  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$  and from tertiary butanol (TBA,  $(\text{CH}_3)_3\text{C}-\text{OH}$ ) via dehydration (see next Sect. 6.3.6.7).

### 6.3.6.7 Higher alcohol synthesis

Higher alcohols are more attractive gasoline blending stocks than methanol. Higher alcohols have a higher heating value, a higher solubility in hydrocarbons, and a lower vapor pressure. There are several processes which can be deployed for higher alcohol synthesis (HAS) from CO and H<sub>2</sub>: the isosynthesis (a variant of Fischer-Tropsch synthesis), oxosynthesis, and homologation of lower-molecular-weight alcohols to higher alcohols. Modified methanol synthesis and Fischer-Tropsch catalysts are used in HAS synthesis, which generally starts from methanol by inserting CO into the CH<sub>3</sub>OH molecule in order to form a C-C bond to produce ethanol. This step is followed by successive steps of complex reactions to produce a mixture of higher alcohols. The general reaction stoichiometry can be written as



The reaction stoichiometry suggests an optimum for CO/H<sub>2</sub> = 2. However, due to the simultaneous occurrence of the shift reaction, the optimum ratio is probably close to 1. The reaction has a poor selectivity and low product yield, the main products being methanol and CO<sub>2</sub>. In a single reactor pass, the yield of alcohols is typically 10% related to syngas conversion, with methanol being the most abundant alcohol produced [00Her]. The synthesis conditions are similar to that used in methanol or FT synthesis. The catalysts are alkali-doped ZnO/Cr<sub>2</sub>O<sub>3</sub>, alkali-doped Cu/ZnO, alkali-doped CuO/CoO/Al<sub>2</sub>O<sub>3</sub>, or alkali-doped sulfides, e.g. MoS<sub>2</sub> or Rh-based catalysts [03Spa]. Between 1935 and 1945, commercially mixed alcohol synthesis from syngas was performed with an alkalinized ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst in Germany.

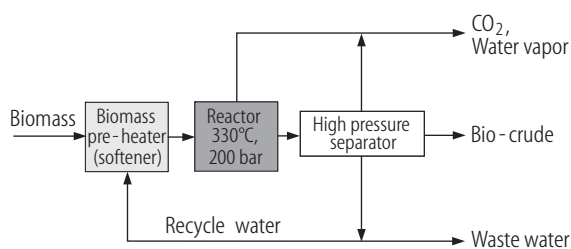
The interest in mixed alcohols as gasoline blends or neat transportation fuels decreased after 1945 with the increasing availability of petroleum products [91For]. Recently, the use of oxygenates as additives to gasoline has revived the interest in HAS. The rapid increase in the demand for MTBE and ETBE led to concerns regarding the shortage of petroleum-derived isobutene. HAS was thus recognized as a possible way to produce oxygenates either by producing alcohols or by using it as a source for MTBE and ETBE. An optimum mixture of methanol and isobutanol ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH) can lead to MTBE. The isobutanol is dehydrated to isobutene which is then combined with methanol to produce MTBE. Considering the current environmental concerns encountered with MTBE, ETBE may attain increased attention in the future. It can be produced in a principally similar way by substituting methanol with ethanol.

### 6.3.6.8 Hydrothermal conversion of biomass

The hydrothermal conversion of biomass using liquid or supercritical water is under investigation in several laboratories. The main advantage of these processes is that they can use wet biomass without drying, which is not the case with most other thermo-chemical biomass conversion technologies. The main problems are related to biomass feeding, system pressurizing, and continuous operation. In the long term, the hydrothermal conversion of biomass may play an important role in the use of biomass with high water content, such as waste biomass streams, fresh plants, etc., which are not suitable for use in conventional thermo-chemical gasification processes.

#### 6.3.6.8.1 The HTU<sup>®</sup> process

Hydrocarbon fuels can be produced by the hydrothermal upgrading (HTU<sup>®</sup>) process with subsequent upgrading of the gained bio-crude by catalytic hydro-deoxygenation (HDO). The process was developed by Shell in the Amsterdam laboratories in the eighties and is based on the conversion of biomass in liquid water (see Fig. 6.3.28). In contrast to gasification technologies, the HTU<sup>®</sup> process is operated at moderate temperatures (300-350°C) and pressures of 150-300 bar.



**Fig. 6.3.28.** Simplified scheme of the HTU<sup>®</sup> process.

Biomass raw materials with high water content serve as suitable materials for this process. The feedstock (soaked and rotted) is mixed with water. The cell structure of the wood is dissolved during this process and subsequent reactions convert the feedstock into a so-called “bio-crude”. A main part of the oxygen in the biomass leaves the reactor as CO<sub>2</sub> (together with some volatile organics), therefore the bio-crude contains less oxygen (10-18 wt-%) than the bio-pyrolysis oil from flash pyrolysis processes (< 40 wt-%). The resulting bio-crude, with an average molecular weight of 300, is not miscible with water, and the lower heating value ranges between 30 and 35 MJ/kg. The effluent water contains dissolved organics and minerals from the biomass feedstock. The thermal efficiency, defined as the lower heating value of the bio-crude product relative to that of the biomass feed (dry basis) plus external fuel and electricity, is 75%, depending on the process configuration [01Gou].

In a downstream hydrogenation process (HDO plant), the oxygen content is further reduced to less than 0.1 wt-%. This oil can be introduced in conventional crude oil refinery processes to be separated into hydrocarbon fuels (gasoline, kerosene, diesel fuel, etc.).

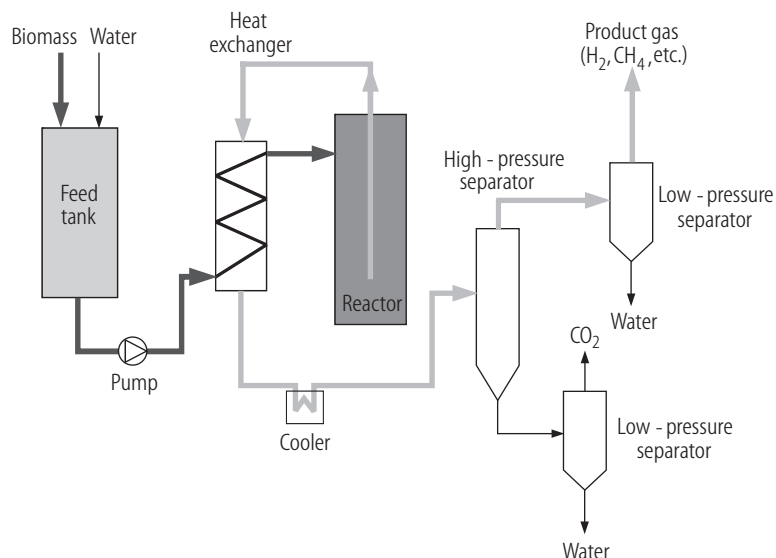
#### 6.3.6.8.2 Conversion of biomass in supercritical water

Supercritical water is obtained at pressures above 221 bar and temperatures above 374°C. When biomass is treated in supercritical water, the organic compounds are converted into fuel gases in the absence of added oxidants and at relatively low temperatures. The gases can easily be separated from the water phase by cooling. The produced high-pressure gas is rich in hydrogen or in methane, depending on the process conditions. A characteristic of the interaction of supercritical water with organics is the gradually changing involvement of water with the temperature. When increasing the temperature to 600°C, water becomes a strong oxidant which results in the complete disintegration of the substrate structure by transferring oxygen from water to the carbon atoms of the substrate.

A schematic presentation of biomass conversion in supercritical water is shown in Fig. 6.3.29. For feeding the process, the educt biomass/water is compressed by a high-pressure pump (with a low energy demand, because the feed is in the liquid phase). The feed is heated up via a heat exchanger and further heated in the reactor. The main reaction products are hydrogen and carbon dioxide as shown in the idealized equation



Side products are methane and small amounts of carbon monoxide. The reaction product is fed to the heat exchanger (heating the feed) and separated from the water phase. CO<sub>2</sub> is dissolved in the high-pressure aqueous phase and can therefore be separated from the combustible gas stream containing mainly H<sub>2</sub> and CH<sub>4</sub>. Possible contaminants such as H<sub>2</sub>S, NH<sub>3</sub>, and HCl are more likely to be captured in the water phase due to their higher solubility, thus in fact providing *in situ* gas cleaning. The process is being transferred from the laboratory to the pilot scale. Pilot plants with ca. 20-30 kg/h biomass were designed and constructed by the Biomass Technology Group (BTG), Netherlands and the Research Center Karlsruhe (FZK), Germany [04Pot], [04Bou].



**Fig. 6.3.29.** Schematic presentation of the pilot plant for biomass gasification in supercritical water [04Bou].

## 6.4 Efficiency of fuel generation

### 6.4.1 Fuel yield per hectare of agricultural crop land

Since the area available for the agricultural cultivation of energy plants is limited, the fuel yield per unit cultivated surface area is of particular importance for fuel production. As apparent in Fig. 6.4.1, there are considerable differences between the production paths of the different fuels with regard to the obtainable yields per area. The yields per area are plotted as the energy obtainable as fuel per hectare and year. The different fuels require different amounts of non-renewable energy for their production. The net yields obtained by subtracting the non-renewable energy share from the gross yields are represented by the second, shorter bars in Fig. 6.4.1. The range of variation is additionally indicated with the net yields [00Dre, 05ZSW]. The highest net fuel yields can be achieved with production methods involving primary gas generation (synthesis gas or bio-gas). The yields per area are lower for methods which use only specific plant parts like oil, sugar, and starch (RME, ethanol). For Central European climate conditions, the values range from ca. 11 MWh ha<sup>-1</sup> a<sup>-1</sup> for bio-diesel from rapeseed up to ca. 40 MWh ha<sup>-1</sup> a<sup>-1</sup> for the production of hydrogen through the thermo-chemical gasification of miscanthus.

The ethanol yield per hectare and year from sugar beet in Europe compared to sugar cane in Brazil does not differ significantly. Two production variants with identical gross fuel yield but different net yields are given for the fuel ethanol. The difference originates from the utilization of the residual and by-products. In one case, bio-gas is produced from the resulting residual material, thereby reducing the input of non-renewable energy. A higher net yield is then possible compared to using the residual material to feed livestock.

In order to indicate the number of vehicles which can be supplied per hectare crop land, we describe two extreme examples with a very high and a very low yield per area and different energy requirements for the automotive drive. Assuming a vehicle with an average consumption of 8 l diesel per 100 km and driven 12000 km a year, one hectare crop land can supply 1.2 vehicles with bio-diesel. For energy-saving vehicles of the future which only consume 3 l diesel-equivalent per 100 km (conventional or fuel cell drive) and the same driving distance per year, 11 vehicles can be supplied with hydrogen produced by the



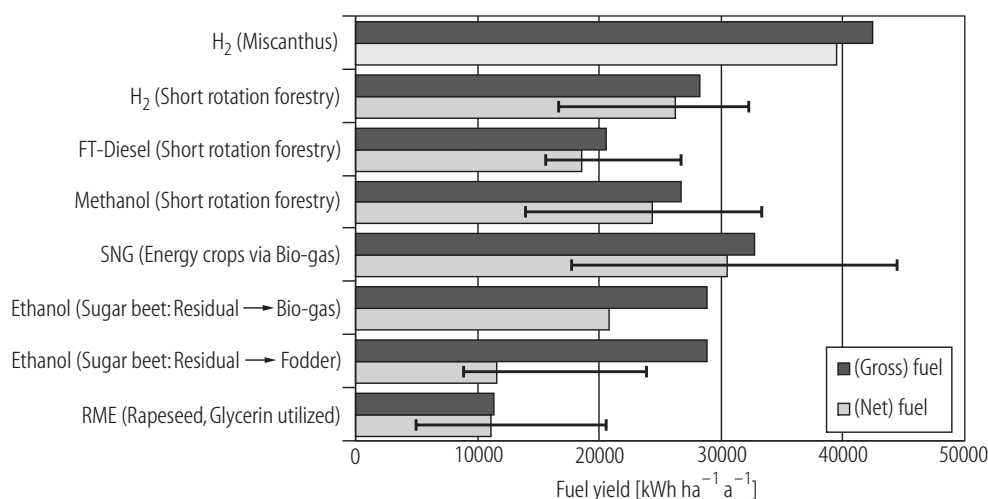
thermo-chemical gasification of miscanthus. This numerical example demonstrates, without fixing an explicit course, that the introduction of “area-efficient” fuels must be accompanied by “energy-efficient” vehicle drives. (For comparison, one hectare of agriculturally cultivated land under Central European climate conditions and for the currently typical consumption habits feeds ca. 5 inhabitants).

### 6.4.2 Energy efficiency of synfuel generation from biomass

One main aspect of fuel generation from renewable sources is the energy efficiency of the overall “biomass-to-synfuel” process chain. The conventional route of transport fuel production from crude oil in refineries shows high conversion efficiencies  $> 85\%$ . This path has the advantage that the fuel production is mainly a physical conversion (rectification) and not a chemical process. The efficiencies decrease in all cases where a chemical conversion process is involved in the fuel production. The production of carbon-based fuels via synthesis gas (syngas) from biomass includes at least two principle chemical conversion steps: syngas generation from biomass and synthetic fuel (synfuel) generation from syngas. Auxiliary processes such as gas cleaning, gas conditioning, production of intermediates, separation, gas compression, etc., also negatively influence the overall energy efficiency. However, plant scale and co-generation aspects can improve the efficiency. Four main factors have been identified as decisive for the energy efficiency of synfuel generation from biomass via synthesis gas:

- 1) The thermodynamics of the different synthesis processes;
- 2) Additional process steps (e.g. gas cleaning and conditioning; decentralized production of intermediates like bio crude oil, Fischer-Tropsch syncrude, etc. for downstream conversion in centralized plants);
- 3) Plant scale;
- 4) Co-generation aspects, e.g. co-generation of electricity, heat, etc.

In this section, the energy efficiency of biomass gasification and fuel synthesis will be discussed, as well as the overall “biomass-to-synfuel” process.



**Fig. 6.4.1.** Fuel yields per hectare and year for various fuel paths – gross and net (less the amount of non-renewable energy required for production) – for Central European climate conditions. The range indicated results from various calculations. H<sub>2</sub> - compressed hydrogen at 250 bar; SNG - substitute natural gas at 250 bar; RME - rapeseed methyl ester.

The first step of the biomass-to-fuel conversion route is the generation of an appropriate synthesis gas in the gasification process. In order to avoid a large inert freight in the synthesis gas, the biomass gasification has to be carried out either allothermal with external heat supplied by a heat exchanger or heat carrier (*indirectly* heated gasifier) or by an autothermal gasification process using oxygen for the partial oxidation of biomass (*directly* heated gasifier). For both indirectly and directly heated gasifiers, a part of the biomass is used to supply heat to the endothermic biomass conversion. (A description of different gasification processes is given in [Sect. 6.3.1](#)).

The main gasification reactions are pyrolysis reactions (degasification of biomass), homogenous gas-phase reactions (like reforming pyrolysis products with steam and CO<sub>2</sub> and including the water-gas shift reaction), the partial oxidation (of the biomass and gaseous components) by oxygen, steam and/or CO<sub>2</sub>, and the simultaneous gasification of solid carbon. The performance of these chemical reactions is limited by the thermodynamic equilibrium. Since this equilibrium is reachable only for infinite residence time of the reactants in the gasifier, the configuration of the gasifier and kinetic aspects have an important influence on the composition of the product gas and the energetic efficiency.

The goal of the gasification process is to convert as much of the biomass as possible into synthesis gas. The gasification process efficiency (cold gas efficiency) is defined as the ratio of the LHV of the (cold) product gas flow to the LHV of the biomass feed flow:

$$\eta_{(\text{cold gas})} = \frac{\dot{V}_{\text{product gas}} \cdot \text{LHV}_{\text{product gas}}}{\dot{m}_{\text{biomass feed}} \cdot \text{LHV}_{\text{biomass feed}}} \quad (6.4.1)$$

LHV represents the lower heating value of the product gas and the biomass feed, while  $\dot{V}$  is the volume flow of the product gas and  $\dot{m}$  is the mass flow of the biomass feed. Auxiliary energy needs for the gasification are not considered in this definition of the cold gas efficiency.

The cold gas efficiency, depending on different parameters like the gasification process, feedstock, moisture content, gasification agent, etc., is in the range of 70-85% [\[02Nus\]](#) and normally does not exceed 85% in a real gasification system based on wood as feedstock. Other authors [\[98Kal\]](#) indicate a higher bandwidth of energetic efficiency with 2-30% loss related to incomplete conversion (carbon in ash and/or liquid by-products), 4-10% heat losses of the reactor and a 4-10% heat loss related to the sensible heat of the product gas. Together these losses correspond to an overall gasification efficiency between 50 and 90%. Upgrading the gasifier raw gas to an appropriate syngas and the subsequent fuel synthesis is accompanied by further energy losses.

The synthesis of fuels from synthesis gas is an exothermic process from the thermodynamic point of view. Table 6.4.1 shows the calculated reaction enthalpy [\[89Bar\]](#) of the fuel synthesis and the efficiencies related to the LHV of the syngas. The figures in Table 6.4.1 show the theoretical limits of the conversion efficiency.

**Table 6.4.1.** Thermodynamic and efficiency calculations for the conversion of syngas to methanol, methane, DME and liquid hydrocarbons (pentane as model substance). Assumptions: stoichiometry factor  $S = 2$  (methanol, DME, pentane),  $S = 3$  (methane), 100% conversion.

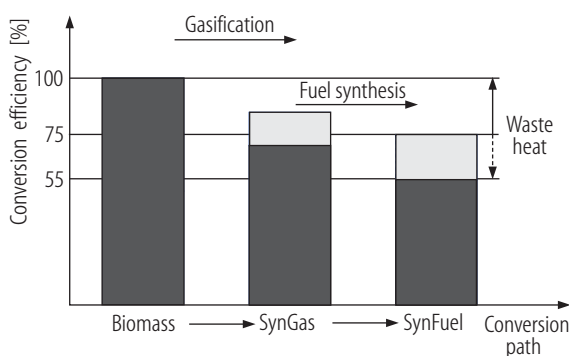
	SYNGAS CO / H <sub>2</sub>		SYNGAS CO <sub>2</sub> / H <sub>2</sub>	
	$\Delta H_{298}$ [kJ/mol]	$\eta = 1 - \frac{\Delta H_{298}}{\text{LHV}_{\text{syngas}}}$	$\Delta H_{298}$ [kJ/mol]	$\eta = 1 - \frac{\Delta H_{298}}{\text{LHV}_{\text{syngas}}}$
CH <sub>3</sub> OH	-90.625	0.882	-49.943	0.931
CH <sub>3</sub> O CH <sub>3</sub>	-204.932	0.866	-121.682	0.916
CH <sub>4</sub>	-206.158	0.796	-165.475	0.829
C <sub>5</sub> H <sub>12</sub>	-802.865	0.803	-602.450	0.844

The assumptions made for the calculations in Table 6.4.1 are: selective processes to the desired products from an adjusted syngas and a 100% carbon conversion. In a real synthesis plant there are several additional up- and downstream process steps, such as syngas and product purification, shift reaction, CO<sub>2</sub> separation and syngas compression, all of which consume energy and lead to a decreased synthesis efficiency. Whereas the energy loss for methanol synthesis from an adjusted H<sub>2</sub>/CO-syngas is about 12%, hydrocarbons and methane synthesis exhibit a theoretical energy loss of 20%. The theoretical energy efficiency for the CO<sub>2</sub>/H<sub>2</sub>-syngas path to synfuels is also presented in Table 6.4.1 for comparison. The use of CO<sub>2</sub> as the carbon source might be a future option for carbon-based fuel synthesis from non-biomass renewable resources.

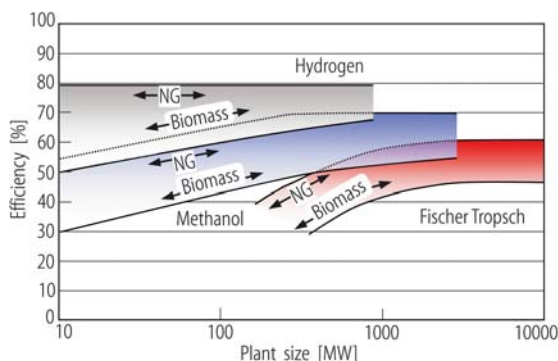
There is a significant difference between the synthesis of the fuels presented in Table 6.4.1 as pure compounds and the Fischer-Tropsch (FT) fuels, which are a mixture of different hydrocarbons. The same is valid for SNG (Substitute Natural Gas), which is not pure methane, but a mixture of different gaseous fuels with CH<sub>4</sub> as a major component. On the other hand, the fuels methanol, dimethyl ether and hydrogen will be used as pure chemical compounds. The synthesis of FT fuels is a two-step process. In a first step, an intermediate product (syncrude) is created, which is converted in a second downstream conversion process into fuels meeting the requirements of the present transportation fuel specifications. Due to this process complexity, the FT fuel synthesis further reduces the overall energy balance of the biomass-to-FT-fuel chain.

Further aspects with a major influence on the energetic efficiency are the syngas-to-synfuel carbon conversion and the co-generation e.g. of electricity. In large-scale plants (> 100 MW<sub>th</sub>) designed for a high synfuel output, the stoichiometry adjustment of the syngas can be close to the ideal. In this case, the biomass conversion path is optimized for a high synfuel output with or without only minor co-generation of electricity. Because syngas conditioning for optimized fuel output is complex and costly, small plants < 10 MW<sub>th</sub> will favor co-generation of synfuel and electricity. The tail gas of a synthesis reactor operating in the once-through mode can then be used for electricity generation. Combining the biomass gasification efficiency (70-85%) and the fuel synthesis efficiency (80-88%) leads to a tentative range for the overall energy efficiency. The results are given in Fig. 6.4.2 in a simplified scheme, showing a maximum conversion efficiency in the range of 55-75% (hatched area). In principle, the waste heat can be used for e.g. steam/electricity generation, drying of feedstock, etc. to increase the overall energy efficiency. However, the main heat requirement, during the endothermic biomass gasification process, can not be covered with recovered heat as a much higher temperature level is necessary for gasification than that provided by the waste heat resulting from fuel synthesis. Therefore, overall efficiencies exceeding the range of 55-75% are considered unrealistic. The following definition is used to compare energy efficiencies of the overall "biomass-to-synfuel" chain:

$$\eta = \frac{\dot{m}_{\text{synfuel}} \cdot \text{LHV}_{\text{synfuel}}}{\dot{m}_{\text{biomass feed}} \cdot \text{LHV}_{\text{biomass feed}} + E_{\text{add. energy demand}}} \quad (6.4.2)$$



**Fig. 6.4.2.** Efficiency of synfuel generation via biomass gasification.



**Fig. 6.4.3.** Estimated efficiency range of the biomass-to-synfuel/hydrogen (lower range of hatched areas) and natural gas-to-synfuel/hydrogen conversion (upper range of hatched areas).

The additional energy demand is mainly auxiliary electric power for different process steps, e.g. syngas compression. A special case is the utilization of hydrogen as an additional feedstock for the process. The combined utilization of biomass and (electrolytic) hydrogen to adjust the stoichiometry of the syngas leads to a considerable increase of fuel output and carbon conversion, but requires a significant amount of (expensive) hydrogen [99Spe2, 95Que].

A further process design is an energetically autarkic conversion plant. This system will include – in addition to the synthesis plant – a power generation plant to supply the electricity requirements of the synthesis or even to export electricity. In this case, the energy efficiency will be calculated as

$$\eta' = \frac{\dot{m}_{\text{synfuel}} \cdot \text{LHV}_{\text{synfuel}} + E_{\text{el, export}}}{\dot{m}_{\text{biomass feed}} \cdot \text{LHV}_{\text{biomass feed}}} \quad (6.4.3)$$

For comparison with literature data, the following must be clarified:

- The definition used for the efficiency calculation (with or without co-generation);
- Whether the additional energy demand is related to the end or to the primary energy (including the conversion efficiency e.g. of electricity generation from fossil fuels);
- Which heating value, LHV or HHV, was considered?

“Biomass-to-synfuel” conversion efficiencies published in the literature include [02Boe, 98Kal, 97Nus, 02Nus, 01Pta, 93Ros, 98Sal, 87Sch2, 01Stu, 02Tij]. The conversion efficiency ranges are represented in Fig. 6.4.3, based on the lower heating value of the produced fuel and the lower heating value of the feed biomass, and including the additional energy demand as end energy. Co-generation of electricity and heat is not considered. Efficiency ranges for natural gas (NG)-to-hydrogen, NG-to-methanol, and NG-to-Fischer-Tropsch fuels are also given for comparison. The efficiency ranges presented for natural gas as feedstock are related to currently existing plants, whereas the efficiencies for biomass as feedstock in Fig. 6.4.3 are based on estimations. It can be concluded from Fig. 6.4.3 that

- 1) depending on the targeted fuel and the plant size, the biomass-to-synfuel and biomass-to-hydrogen conversion efficiencies range from 30-80%;
- 2) the energetic efficiencies for  $\text{H}_2$  and methanol are higher than for Fischer-Tropsch fuels;
- 3) the energetic efficiency increases with plant size;
- 4) in order to achieve acceptable efficiencies for FT fuels, large-scale plants are indispensable.

## 6.5 Resources for the production of renewable fuels

Different technologies are available for introducing renewable energy into the transportation sector – based on biomass, renewable electricity, and the combination of both resources. In this chapter, a short overview will be given regarding the principle resources for renewable fuel production.

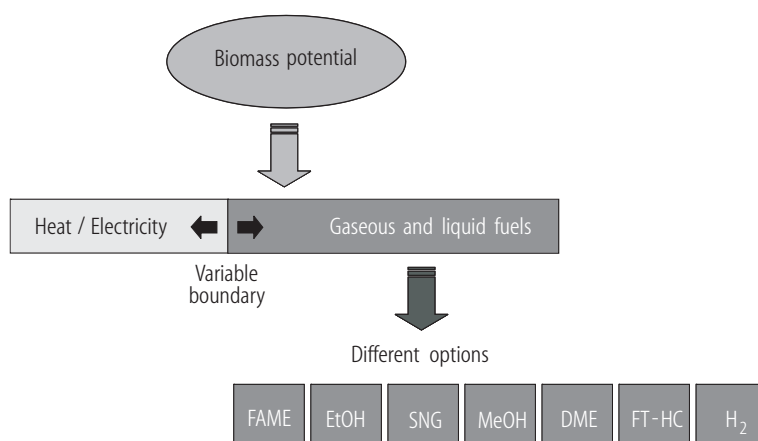
The introduction of renewable energy for fuel generation is indispensable in a long-term strategy. There is no question about the finite availability of fossil resources, especially crude oil, for transport fuel production. The number of new oil strikes has been decreasing continuously over the last decades. According to most current studies about fossil resources for fuel production, the “mid-depletion point” is expected in one or two decades.

### 6.5.1 Biomass resources

Several options are available for the energetic use of biomass – ranging from the generation of heat or electricity through combustion to the production of solid, liquid, or gaseous fuels for use in co-generation plants or for the transportation sector. The question arises of when the various sectors will compete for the bio-energy carriers, and how to set the priorities when the time comes. The biomass potential consists of very different primary materials which are not equally suitable for all conversion methods. Therefore, a division of potential will occur, adjusting to the prevailing technical and economic conditions. Energy-political factors also play a role, but once established they are very difficult to change.

It is not yet clear which portion of the biomass potential will be used in the future for the generation of electricity and heat, and which portion will be used for the production of gaseous and liquid fuels (Fig. 6.5.1). Various studies about biomass potentials estimate the total proportion for fuel production to be 50%. Important criteria for considering the division of potential are as follows:

- Specifications for the construction of new supply structures in the heat market;
- Diversification of the energy carriers for transportation;
- Spatial distribution of the biomass sources;
- Availability of carbon apart from fossil resources (biomass is the only regenerative energy carrier which contains concentrated carbon);
- CO<sub>2</sub> reduction potential of the various utilization paths;
- Costs of the biomass conversion;
- Existing political objectives (e.g. doubling goal for renewable energy, development goal for the use of biomass in fuel production [01EUC]).



**Fig. 6.5.1.** Technical biomass potential and usage options in the heat, electricity, and fuel sectors. (see Glossary in [Sect. 6.8](#) for abbreviations).

The world biomass potential can be only roughly estimated due to limitations in the available data. The situation is complicated by the fact that the biomass fluxes are evaluated very differently in many cases. In general, there are two types of potentials portrayed in different biomass records: the theoretical and the technical potential. The theoretical potential describes the theoretical, physically available biomass energy in a given region over a certain period of time.

A global analysis regarding the biomass potential for fuel production shows that the theoretical biomass potential can be calculated to  $2.88 \cdot 10^{21}$  J/a (world-wide physical potential) with an average specific biomass growth [00Dre]. This value is about eight times the total world primary energy consumption. The technical potential indicates the part of the theoretical potential which is exploitable in the frame of given technical conditions. The technical potential can be derived from the theoretical potential by applying the following limiting factors:

- Availability of biomass resources (e.g. priority claim for food production);
- Preservation of natural cycles (e.g. humus balance);
- Ecological limitations (e.g. sustainable forestry);
- Technical limitations;
- Space- and time-related diversity of supply and demand.

The volume of resources from agriculture and forestry are very difficult to estimate due to the following factors [94WEC]:

- The statistics on harvest production and consumption of wood and straw are inadequate or totally absent.
- The production levels from agriculture and forestry depend on the climate, consequently resulting in large variations from year to year, and region to region.
- The market for agricultural and forestry products depends on market forces, and therefore the amounts to be used for energy purposes depend heavily on the price of the energy feedstock.
- The amounts available from the different sectors (agriculture, forestry, waste sector) interact in a complex way.

The world-wide technical biomass potential can be divided into primary biomass (energy plants) and secondary biomass (rest biomass in the form of waste wood from forestry and industry, harvest residues, etc.). Whereas the potential of the secondary biomass is reliably estimated to be about 50 EJ/a (e.g. 45 EJ/a [00Dre], 65 EJ/a [01Kal]), there is a great uncertainty about the available primary biomass potential, which mainly depends on the available agriculture area and the species of energy crops considered. Calculations range from 82 EJ/a [01FNR] to 260 EJ/a [97IEA]. The 260 EJ/a calculation is based on an assumed agriculture area of  $8.9 \cdot 10^8$  ha (the area for food production sums up to about  $1.4 \cdot 10^9$  ha today). Furthermore, it assumes that the plantations yield an average of 15 dry tons per hectare per year, with a heating value of 20 GJ per ton. Many decades would be necessary to establish energy plantations on this scale. For comparison, in 1999 the total world-wide primary energy consumption was 406.2 EJ/a, and the utilization of combustible biomass and waste for energetic applications was 45 EJ/a [01IEA]. With currently 11%, biomass contributes more to the global primary energy consumption than any other renewable resource.

The world-wide consumption of transportation fuels summed up to about 70 EJ/a in 1999, whereof 54.0% is for gasoline, 33.1% for diesel, and 12.9% for aviation fuel [01IEA]. The production of renewable fuel competes with other forms of biomass use, such as heating and electricity production. Therefore, the technical potential does not necessarily reflect the availability of biomass under given socio-economic conditions in different countries of the world. Only part of the technical biomass potential can be used for the production of regenerative fuels. Material fluxes for the generation of heating and electricity which are already established or foreseeable must also be considered. Such cases include traditional structures like the private use of wood and the wood-working and wood-processing industries. Even with all these uncertainties and restrictions, and assuming that only a part of the biomass is available for transportation fuel production, it is clear that biomass may contribute substantially to fuel production in the future.

In the long term, the importation of renewable electricity via a high-voltage grid is a further option to power the electrolysis of water for hydrogen generation directly at the fuel production site (see

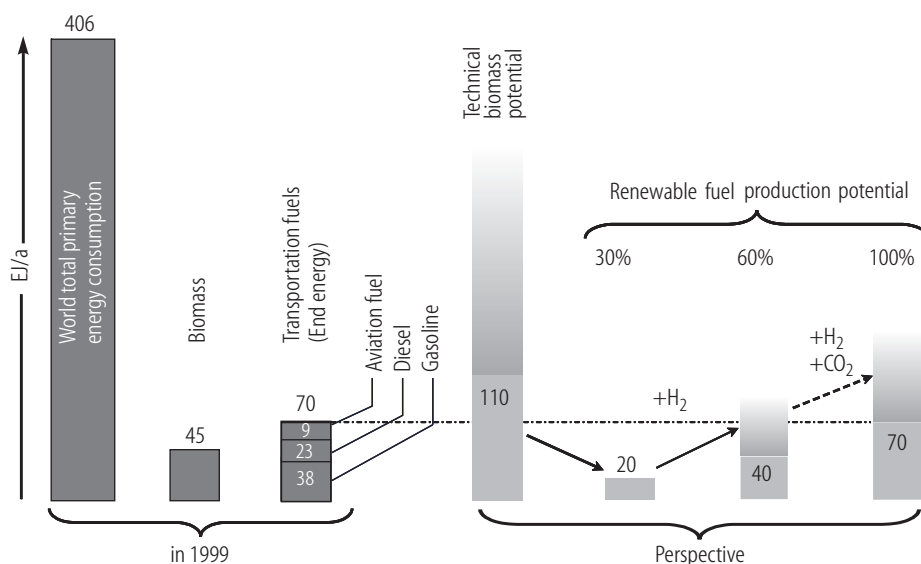
Fig. 6.5.2). Using biomass for fuel production via gasification produces synthesis gas containing a large excess of carbon. The stoichiometry can be adjusted by either adding (renewable) hydrogen or by removing carbon in the form of carbon dioxide. The addition of hydrogen allows the use of nearly all of the carbon contained in the biomass, resulting in a high fuel production rate.

Due to all the uncertainties in the biomass potential records around the world, the resulting world biomass potential should be considered carefully. Assuming a minimum technical biomass potential of 110 EJ/a, and a “free” potential of about 65 EJ/a from which 60% is available for transport fuel production with an energetic efficiency of 50%, it can be concluded that approximately 30% of the total world transportation fuel consumption, based on the consumption today, can be covered (Fig. 6.5.2). If renewable hydrogen is available for the synthesis process, this share increases up to about 60%. Using renewable hydrogen and  $\text{CO}_2$  as the long-term carbon source for fuel synthesis, it will be possible to cover the overall fuel requirement using renewable sources in the future. The utilization of  $\text{CO}_2$  represents a carbon source for fuel synthesis which is not limited by biomass resources. The combined utilization of

- 1) biomass resources,
- 2) renewable electricity for hydrogen generation, and
- 3)  $\text{CO}_2$  as a long-term carbon source

offers in principle the possibility for a completely renewable carbonaceous fuel supply in the future.

To which extent the resources will be utilized depends on numerous conditions, not the least on the costs. The following describes an example for Germany, since strong figures are accessible for this country. Figure 6.5.3 demonstrates the cost-potential curve for the “free” usage potential, correlated with present and foreseeable supply costs. Appreciable potentials for mobile applications can be found for liquid manure and straw residue from the agricultural industry (a total of ca. 200 PJ/a). The potentials for forest wood residue and energy plants are about twice as large, but also significantly more expensive at up to 2 €/kWh. Assuming a 50% degree of conversion when producing regenerative fuels from biomass, the biomass cost share alone adds up to ca. 0.40 € per liter gasoline equivalent.



**Fig. 6.5.2.** Comparison of the world-wide primary energy consumption and the transportation fuel demand with the technical potential of energetic biomass resources for renewable fuel generation. The percentage of renewable fuels can be increased by using additional hydrogen and carbon dioxide for the fuel production process. (Assumptions: available biomass 110 EJ/a; 60% share for transport fuel production; renewable fuel production potential in % of the transportation fuel demand in 1999).



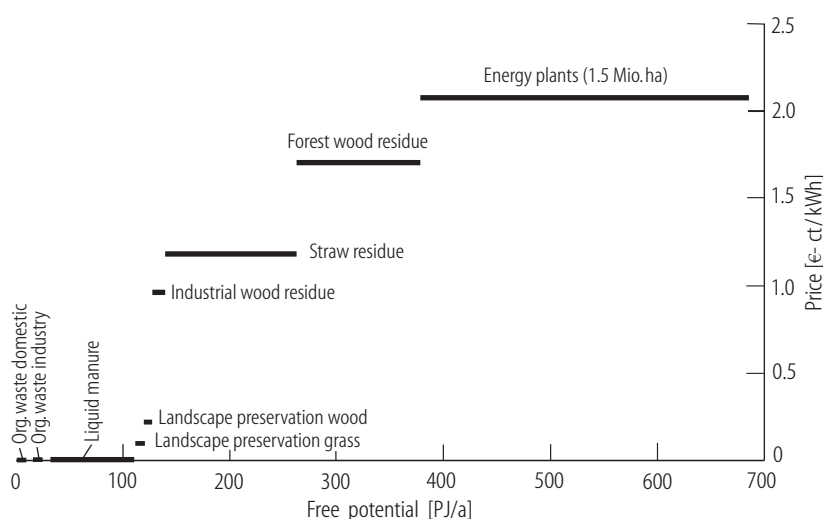
**Table 6.5.1.** German, European, and world-wide substitution potentials for regenerative fuels from biomass.

	Germany	EU-15	EU-27 <sup>3)</sup>	World
Fuel consumption [EJ/a] <sup>1)</sup>	2.7	10.5	12.0	70.2
Technical biomass potential [EJ/a]	1.2	6.8	8.9	109.0
“Free” biomass potential [EJ/a]	0.7	4.6	6.9	63.8
Factor “fraction × efficiency” <sup>2)</sup>	0.25	0.25	0.3	0.3
Fuel substitution potential [EJ/a]	0.2	1.2	2.1	19.1
Fuel substitution potential [%]	7	11	18	27

<sup>1)</sup> Fuel consumption in the transportation sector (1999).

<sup>2)</sup> The factor “fraction × efficiency” accounts for the fraction of biomass which is used for fuel production and the energetic efficiency of the conversion.

<sup>3)</sup> Including Romania and Bulgaria.

**Fig. 6.5.3.** Cost-potential curve for the “free” biomass potential in Germany.

Based on today’s fuel consumption in Germany, together with the assumption that 50% of the “free” biomass potential is used for the production of fuels with an average energetic efficiency of 50% (factor “fraction × efficiency” = 0.25), a substitution potential of 7% can be calculated (see Table 6.5.1). The factor “fraction × efficiency” accounts for the fraction of the biomass which can be used for fuel production together with the conversion efficiency from primary resource to fuel. The slightly higher factor in the columns “EU-27” and “World” indicates the ratio between biomass presence and population density. As a result of limited transportation paths and a lower consumption level, more biogene resources are available for fuel production in regions with lower population densities. Due to their much higher energy density, the regenerative fuels are easier to transport than the biomass from which they are produced.

The world-wide “free” biomass potential is also strongly reduced by the consumption of biomass for energy purposes (especially in countries of the Third World). With ca. 45 EJ/a, biomass currently contributes about 11% to the world primary energy consumption [01IEA]. The world-wide fuel consumption in the transportation sector is 70.2 EJ/a. For comparison, estimations of the biomass potential and the resulting fuel substitution potential are also given for the EU-15 (11%), the EU-27 (18%), and world-wide (27%) in Table 6.5.1. In order to reach a 5.75% of bio-fuel in the transport sector (the European Union target quota for 2010 [01EUC]), about 16-40% of agricultural land would be necessary for the EU-15, and 12-23% for the EU-27, respectively [04Kav]. Only part of the fuel requirement can be met with bio-

mass-derived resources at the current consumption levels, especially for industrialized countries with a high level of energy consumption and limited agricultural acreage.

The percentage of substitution potential can be considerably increased if the supply of regenerative fuels is coupled with an increase of efficiency and/or decrease of consumption for the vehicle drives (e.g. “3-liter car”). These conditions exist, especially in countries like Germany which have a declining fuel consumption in the transportation sector. On the other hand, the world-wide consumption is rising due to the strongly increasing traffic volume traffic, which, at least in the short term, cannot be compensated for with improved efficiency.

### 6.5.2 Renewable electricity for fuel generation

The availability of renewable electricity is of vital importance for the generation of regenerative fuels. Here the emphasis does not lie on the electrolytic generation of hydrogen for load control within the electricity supply, but rather the generation or the importation of regenerative electricity. The electrolytic production of hydrogen to dampen fluctuations in the regenerative electricity supply is at best a relevant aspect in the long term. No surpluses are expected in Europe for regenerative electricity shares up to about 30% [00Nit]. Also for other countries, surplus electricity will only be available once similarly high values for the share of regenerative electricity are exceeded.

In the long term, it will be possible to increase the share of renewable energy carriers by importing renewable electricity via a high-voltage grid. Already today, some countries (e.g. Norway and Iceland) can only access their renewable energy potential by exporting electricity or developing energy-intensive industries, since these countries utilize almost exclusively regenerative electricity. Exemplary technical potentials for the possible importation of regenerative electricity are listed in the following [00Nit]:

- Wind power Europe: 400-3000 TWh/a;
- Wind power Morocco: 300-600 TWh/a;
- Hydropower Norway: 60 TWh/a;
- Hydropower Iceland 30 TWh/a;
- Hydropower CIS: 1300 TWh/a;
- Solar electricity from North Africa: > 106 TWh/a.

For comparison, the German electricity consumption was 596 TWh/a in 2003 [05AGE], and the world-wide electricity consumption was 14701 TWh/a in 2002 [04IEA1].

There is an enormous potential for solar electricity production in North Africa which can be accessed with solar thermal and, where appropriate, photovoltaic power plants. Just 1% of the useful technical potential in the region could theoretically meet today’s entire world electricity requirement. Of course, it is not reasonable to concentrate on one single resource. However, the numerical example indicates the large significance of this region for the future regenerative electricity supply in Europe as part of a North-South co-operation. Furthermore, exporting regenerative electricity is also associated with developing the economy and infrastructure of the regions concerned.

Regenerative electricity can be used to produce electrolytic hydrogen, which can then be utilized in three different ways:

- 1) Hydrogen can be used directly as a secondary energy carrier.
- 2) Hydrogen can meet the hydrogen deficit in synthesis gas from biomass for carbonaceous fuel production. Since the H<sub>2</sub> content is too low in biomass-derived synthesis gas, the amount of fuel produced from it can be multiplied by adding electrolytically produced hydrogen. For example, the amount of methanol synthesized using a biomass gasification process can be tripled by adding H<sub>2</sub> [99Spe2]. The integration of additional hydrogen thus offers the possibility to achieve a high level of conversion from biomass carbon to fuel carbon (> 80%).
- 3) Hydrogen and carbon dioxide can be used as educts for the synthesis of carbonaceous fuels (without using biogene resources as the carbon source).

## 6.6 Conclusions / Outlook

High CO<sub>2</sub> reductions exceeding 90% are possible using regenerative fuels – reductions which could not be achieved solely by improving the efficiency of the automotive drive assembly. Although the availability of biogene resources for the production of regenerative fuels is limited, they can still meet appreciable shares of up to 30% world-wide (referred to the current fuel consumption for transportation). In the long term, regeneratively produced electricity will also come into consideration for the production of fuels.

How will the shares of different regenerative fuels be distributed over the total consumption in the future? Which regenerative fuel will achieve market penetration depends, among other things, on the amount of CO<sub>2</sub> emissions avoided, on the costs of avoiding CO<sub>2</sub>, and on the availability of the various technologies.

A significant factor determining when regenerative fuels will be used in large scale is the “ecological efficiency” of the employed regenerative resources. This factor depends on the extent to which CO<sub>2</sub> emissions or other environmental impacts can be avoided through the use of regenerative fuels. For example, whereas one kWh of electricity in Germany’s strongly coal-based system leads to the release of about 0.7 kg CO<sub>2</sub>, one kWh gasoline or diesel produces only about 0.3 kg CO<sub>2</sub>. Therefore, from the aspect of climate protection, substituting conventional electricity with regenerative electricity is more than twice as efficient as substituting conventional fuels. In this respect, however, the optimal implementation of regenerative fuels for transportation is just a matter of time. On the one hand, the increasing penetration of climate-neutral energy carriers in the utilities pool and the substitution of coal with natural gas lead to declining specific CO<sub>2</sub> emissions from electricity generation. This reduction is slowed, however, in those countries planning to phase out nuclear energy. On the other hand, gasoline and diesel fuels will lead to higher emissions as a result of the increasing shortage of resources and additional conversion steps (synthetic fuels from natural gas or coal), and also due to the escalating requirements on the chemical composition of the fuels. The use of renewable energy carriers is therefore deemed necessary, and least in the long term, for reasons of ecological efficiency.

The use of regenerative fuels cannot currently be justified with the costs of avoiding climate-relevant gases alone, since avoiding CO<sub>2</sub> in the transportation sector is particularly expensive. In the future, however, every energy-consuming sector, including transportation, will have to contribute to the reduction of climate-relevant emissions. Indeed, the future price trends are strategically significant for the evaluation of regenerative primary energy carriers in the transportation sector. A relative shift in the price trends for the mobile and stationary sectors, caused for example by the disproportionate rise in the cost of crude oil due to the depletion of resources and shortage in supply, can result in a shift of the point in time when the use in the mobile sector becomes more attractive. A study from Prognos [01Sch] assumes that the price of crude oil will triple by 2050, while the price of electricity will moderately increase. Such a trend will make the substitution of crude-oil-based fuels more attractive in the future.

Further aspects besides the criteria for CO<sub>2</sub> avoidance also play a role in the introduction of regenerative fuels. If these aspects include the diversification of resources and the security of supply, then other preferences result when evaluating regenerative energy carriers. Whereas a multitude of substitution possibilities are available in the electricity and heating markets, it is much more difficult to reduce the dependency on crude oil in the transportation sector. Precisely this fact is a strong argument for the increased use of regenerative primary energy in the production of fuels.

Due to the existing infrastructure, bio-diesel (pure or as an additive of up to 5 vol-% to conventional diesel fuel) and ethanol (as an additive of up to 5 vol-% to gasoline or for the production of the “octane booster” ETBE) will be the first fuels to gain market shares. Owing to the relatively low net acreage yields of ca. 11 MWh ha<sup>-1</sup> a<sup>-1</sup>, the growth potential for bio-diesel (and also for ethanol, depending on the production method) is, however, limited. In the medium term, synthetic fuels – along with substitute natural gas from bio-gas – will experience increased market penetration once biomass-adjusted conversion technologies are successfully established. Hydrogen is only expected to gain significant shares in the very long term (> 2050?), since the infrastructure requirements represent a sizeable economic challenge.

## 6.7 Additional tables

### 6.7.1 Promising renewable neat fuels and blends for automotive applications

Neat fuels	Utilization as transport fuel
Bio-diesel (FAME) / B100	Diesel engines with warranty for bio-diesel
Bio-pyrolysis oil	Intermediate energy carrier; not qualified as transport fuel
DME	Dedicated DME diesel engines
EtOH / E100	Dedicated ICEs
H <sub>2</sub>	Dedicated ICEs and fuel cells
MeOH / M100	Dedicated ICEs (Otto and diesel) and fuel cells
SVO	Adapted diesel engines
SNG	All NG vehicles
Synthetic diesel	Existing diesel engines and dedicated ICEs
Synthetic gasoline	Existing Otto engines

Blends with conventional fuels	Utilization as transport fuel
B5 (5 vol-% bio-diesel in diesel)	All existing vehicles with diesel engines
E5 (5 vol-% EtOH in gasoline)	All existing vehicles with gasoline engines
E10 (10 vol-% EtOH in gasoline)	All gasoline cars in USA can use E10 (E10 = "gasohol")
E22 (22 vol-% EtOH in gasoline)	All gasoline cars in Brazil can use E22 (common gasoline in Brazil)
E85 (85 vol-% EtOH in gasoline)	Ethanol flexible fuel vehicles (FFV), FFVs are also able to run on gasoline and any mixture between gasoline and E85
E95 (95 vol-% EtOH in gasoline)	Dedicated ICEs
ETBE (< 15 vol-% in gasoline)	All existing vehicles with Otto engines
EtOH in diesel ("diesohol", < 15 vol-% of (hydrated) EtOH in diesel)	Vehicles with diesel engine (no or little engine modification; an emulsifier is necessary to form an emulsion)
H <sub>2</sub> (< 20 vol-%) in NG	Adapted NG ICEs
M3 (3 vol-% MeOH in gasoline)	Existing vehicles with Otto engines (a dissolving agent, e.g. TBA, is necessary to avoid phase separation)
M15 (15 vol-% MeOH in gasoline)	Vehicles with modified Otto engines
M85 (85 vol-% MeOH in gasoline)	MeOH flexible fuel vehicles (FFV)
MeOH in diesel ("diesohol", < 15 vol-% of (hydrated) MeOH in diesel)	Vehicles with diesel engine (no or little engine modification; an emulsifier is necessary to form an emulsion)
MTBE (< 15 vol-% in gasoline)	All existing vehicles with Otto engines
SVO in diesel	Adapted diesel engines
SNG in NG (0-100 vol-%)	All NG vehicles
Synthetic diesel in conventional diesel (0-100 vol-%)	All existing vehicles with diesel engines
Synthetic gasoline in conventional gasoline (0-100 vol-%)	All existing vehicles with Otto engines

### 6.7.2 Fuel Properties of selected liquid and gaseous fuels

Liquid fuel	Chem. formula	Density [kg/m <sup>3</sup> ]	Boiling tem- perature [°C]	LHV [kWh/kg]	LHV [kWh/l]
Gasoline	C5 - C12 compounds	715-780	25-215	11.9-12.1	9.1
Kerosene	C9 - C16 compounds	770-830	170-260	11.9	9.7-10.0
Diesel	C10 - C23 compounds	815-855	170-380	11.8	9.9
FT-diesel	C10 - C23 compounds	770-860	150-320	12.4	9.9
Plant oil (rapeseed)	Glycerine ester	910-920	> 240	10.6	9.7
FAME (RME)	R-CO-O-CH <sub>3</sub>	870-880	330 - 350	10.3-10.5	9.0-9.2
Methanol	CH <sub>3</sub> OH	791	64.7	5.47	4.33
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	794	78.5	7.44	5.91
MTBE	(CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub>	741	55.2	9.8	7.3
ETBE	(CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>2</sub> CH <sub>3</sub>	752	71	10.0	7.5

Gaseous fuel	Chem. formula	Density [kg/m <sup>3</sup> ]	Boiling tempera- ture [°C]	LHV [kWh/kg]	LHV [kWh/l]
Hydrogen	H <sub>2</sub>	0.0899	-252.8	33.3	3.0 [kWh/m <sup>3</sup> ]
Hydrogen (liquid)		70.9			2.36
Hydrogen (200 bar)		15.8			0.53
Methane	CH <sub>4</sub>	0.718	-161.5	13.9	9.97 [kWh/m <sup>3</sup> ]
Methane (200 bar)		135			1.78
Propane	C <sub>3</sub> H <sub>8</sub>	1.87	-42.1	12.9	25.99 [kWh/m <sup>3</sup> ]
Propane (liquid)		501			7.5
Butane	C <sub>4</sub> H <sub>10</sub>	2.52	-0.5 (n-Butane) -11.7 (i-Butane)	12.7	34.32 [kWh/m <sup>3</sup> ]
Butane (liquid)		601			7.7
DME	CH <sub>3</sub> -O-CH <sub>3</sub>	1.8	-24.9	7.9	14.2 [kWh/m <sup>3</sup> ]
DME (liquid)		668			5.2

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## 6.8 Glossary and abbreviations

AER	Absorption-enhanced reforming
Allothermal	The energy for the endothermal gasification reaction is introduced externally into the gasification chamber by means of a heat exchanger or a heat carrier
Autothermal	The energy for the endothermal gasification reaction is introduced directly into the process through a partial combustion of the reactants.
B5	Blend of 5 vol-% bio-diesel in petroleum diesel fuel
B100	100 vol-% bio-diesel
BFB	Bubbling fluidized bed process
Bio-crude	Product of the HTU <sup>®</sup> process
Bio-diesel	See FAME
Bio-fuel	Renewable fuel produced from biomass
Bio-gas	Gas produced via anaerobic digestion of biomass containing mainly CH <sub>4</sub> and CO <sub>2</sub>
Bio-methanol	Methanol produced from biomass
Bio-oil	Bio-pyrolysis oil or bio-crude
Bio-pyrolysis oil	Condensed product gas of biomass flash pyrolysis
Bio-syngas	Synthesis gas via biomass gasification (or bio-gas reforming)
BTL	Biomass-to-liquids
Cetane number	Measure for the ignition quality of a diesel fuel
CFB	Circulating fluidized bed process
CGH <sub>2</sub>	Compressed gaseous hydrogen
CHP	Combined heat and power
CIS	Commonwealth of Independent States
CNG	Compressed natural gas
DME	Dimethyl ether
DMFC	Direct methanol fuel cell
E5	Blend of 5 vol-% ethanol in gasoline fuel
E22	Blend of 22 vol-% ethanol in gasoline fuel
E85	Fuel with 85 vol-% ethanol (rest gasoline)
E95	Fuel with 95 vol-% ethanol (rest gasoline)
E100	Neat ethanol
ETBE	Ethyl tertiary butyl ether (CH <sub>3</sub> ) <sub>3</sub> C-O-C <sub>2</sub> H <sub>5</sub> produced from EtOH and isobutene, octane booster to improve knock resistance of gasoline
EtOH	Ethanol
EU-15	European Union, 15 member states
EU-25	European Union, 25 member states
EU-27	European Union, 25 member states + Romania + Bulgaria
FAME	Fatty acid methyl ester (bio-diesel)
FB	Fluidized bed process
FFV	Flexible fuel vehicle, i.e. vehicle able to drive on any mixture of alcohol (MeOH or EtOH) and gasoline up to 85 vol-% alcohol
FT-fuel	Fischer-Tropsch fuel
FT-HC	Fischer-Tropsch hydrocarbons
FT-synthesis	Fischer-Tropsch synthesis
FICFB	Fast internally fluidized bed process (biomass gasification process of Vienna Technical University)
GHG	Greenhouse gas
GH <sub>2</sub>	Gaseous hydrogen
GTL	Gas-to-liquids
ha	Hectare
HAS	Higher alcohol synthesis

HHV	Higher heating value
HTU	Hydro thermal upgrading
HTW	High-temperature Winkler process
Hythane	Mixture of (typically 5 vol-%) hydrogen in methane
kWh	Kilowatt-hour
ICE	Internal combustion engine
IGCC	Integrated-gasification combined-cycle (power generation)
LH <sub>2</sub>	Liquid hydrogen
LHV	Lower heating value
LNG	Liquid natural gas
LPG	Liquefied petroleum gas (mixture of propane/butane)
LPMEOH™	Liquid phase methanol synthesis (trademark of Air Products and Eastman Chemical Company)
M3	Blend of 3 vol-% methanol in gasoline fuel
M85	Fuel with 85 vol-% methanol (rest gasoline)
M100	Neat methanol
MeOH	Methanol
MSR	Methane steam reforming
MTBE	Methyl tertiary butyl ether (CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub> produced from MeOH and isobutene, octane booster to improve knock resistance of gasoline
MTG	(Mobil) Methanol-to-gasoline process
MTO	Methanol-to-olefins process
MTP	Methanol-to-propylene process
MTSynfuels	Methanol-to-synfuels process
NG	Natural gas
Nm <sup>3</sup>	Norm cubic meter (0°C; 1.013 bar)
NMHC	Non-methane hydrocarbons
NTP	Normal temperature and pressure (0°C; 1.013 bar)
OM	Organic matter
PEMFC	Polymer electrolyte membrane fuel cell
plant oil	Vegetable oils gained from different seeds (e.g. rapeseed, sunflower, soybean)
ppmv	Parts per million by volume
PME	Plant oil methyl ester
PSA	Pressure swing adsorption
PV	Photovoltaic
RE	Renewable energy
RME	Rapeseed oil methyl ester
<i>S</i>	Stoichiometric factor; $S = (p_{H_2} - p_{CO_2}) / (p_{CO} + p_{CO_2})$
Space-time-yield	$\text{kg}_{\text{product}} \text{ l}_{\text{catalyst}}^{-1} \text{ h}^{-1}$
Space velocity	$\text{l}_{\text{educt gas}} \text{ l}_{\text{catalyst}}^{-1} \text{ h}^{-1}$
SMDS	Shell middle distillate synthesis process
SNG	Substitute (synthetic) natural gas
SPD	Slurry phase distillate process of SASOL
SVO	Straight vegetable oil (plant oil)
Syncrude	Wax-rich primary product of Fischer-Tropsch synthesis
Synfuel	Synthetic fuel
Syngas	Synthesis gas (H <sub>2</sub> , CO, CO <sub>2</sub> )
TBA	Tertiary butanol, (CH <sub>3</sub> ) <sub>3</sub> C-OH
THC	Total hydrocarbons
Trans-esterification	Original fatty acid ester with glycerine is split into fatty acid and glycerine. The fatty acid reacts with the methanol added to the solution yielding the bio-diesel.
“Well to tank”	CO <sub>2</sub> emissions, energy demand, etc. in the system chain from “well to tank”
“Well to wheel”	CO <sub>2</sub> emissions, energy demand, etc. in the entire system chain from “well to wheel”



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