SYNTHESIS GAS FROM BIOMASS
for fuels and chemicals

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Acknowledgement/Preface

This report is the result of the workshop “Hydrogen and synthesis gas for fuels and chemicals” organised by IEA bioenergy Task 33 (biomass gasification) in conjunction with the SYNBIOS conference held in May 2005 in Stockholm, Sweden. The authors added extra information where necessary to get a more complete picture.

Key words

gasification, synthesis gas, syngas, biofuels, chemicals

Abstract

Making H₂ and CO (syngas) from biomass is widely recognised as a necessary step in the production of various second generation biofuels. There are two major ways to produce a bio-syngas: fluidised bed gasification with catalytic reformer or entrained flow gasification. The latter option requires extensive pre-treatment such as flash pyrolysis, slow pyrolysis, torrefaction, or fluidized bed gasification at a low temperature. Cleaned and conditioned bio-syngas can be used to synthesize second generation biofuels such as Fischer-Tropsch fuels, methanol, DME, mixed alcohols, and even pure hydrogen. The report describes the different technical options to produce, clean and condition bio-syngas. Furthermore, issues related to scale and biomass transport are covered shortly.
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Summary

Biofuels are expected to become increasingly important in the future to reduce CO$_2$-emissions, improve local emissions, and obtain security of supply. Much RD&D efforts worldwide focus on ways to produce so-called second generation biofuels, that are characterised by excellent environmental performance as well as high biomass feedstock flexibility. Producing H$_2$ and CO (syngas) from biomass is a crucial step in the production of most second generation biofuels.

There are two major approaches to convert biomass into syngas: (1) fluidised bed gasification with subsequent catalytic reforming, both operating around 900°C, and (2) entrained flow gasification at approximately 1300°C with extensive pre-treatment.

The fluidised bed gasification approach has the advantage that the gasification technology has been developed and already demonstrated with biomass for the production of heat and/or electricity. RD&D therefore mainly focuses on downstream catalytic reforming. Entrained flow gasification processes have already been developed and demonstrated on large-scale for coal. Biomass feedstock however, needs to be pre-treated in order to take full advantage of the coal-based technologies. RD&D therefore focuses on pre-treatment such as flash pyrolysis for the production of a high energy density slurry and torrefaction for the production of a “bio-coal”. Close-coupled pre-treatment options include slow pyrolysis (500°C) and fluidised bed gasification (600-900°C).

Raw syngas must be cleaned and conditioned extensively in order to meet the specifications of catalytic synthesis processes like Fischer-Tropsch, methanol, and DME synthesis. Technologies will however be relatively conventional and most often will comprise filters, Rectisol unit, and gas polishing by e.g. ZnO and active carbon filters. A water gas shift reactor and CO$_2$-removal unit generally should be included.

The scale of the plants is an important issue. The back-end of the process (fuel synthesis) generally needs to be as large as possible because of the dominant economy-of-scale effect in biofuel synthesis and upgrading. The front-end however involves biomass supply, which generally means that increasing plant size concern higher feedstock costs because longer transport distances are involved. The scale “mismatch” can be overcome by (1) splitting the processes by producing an easy to transport biomass-based intermediate product like slurry or “bio-coal”, or (2) advanced process integration in order to increase efficiency and reduce overall costs. This last option includes the combination of black liquor gasification, biofuel production and chemicals recovery in a pulp and paper mill, which typically does not exceed 400-600 MW$_{th}$ biomass input capacity.
1. Introduction

1.1 IEA

The International Energy Agency (IEA) comprises different agreements amongst which the Bioenergy Agreement. Within this agreement, Task 33 deals with biomass gasification. Twelve countries are members of this task. More information is available at www.gastechnology.org/iea. Information exchange between the members is achieved by having two meetings each year. This includes a workshop covering a specific topic that is of interest of the Task 33 members. This document reports on the workshop “Hydrogen and synthesis gas for fuels and chemicals” held in conjunction with the international conference SYNBIOS.

1.2 SYNBIOS

SYNBIOS is the name of the conference with subtitles “The syngas route to automotive biofuels” and “Second generation automotive biofuel conference”. It has been organized by Ecotraffic and Nycomb Synergetics AB, both located in Stockholm. The SYNBIOS conference was held in Stockholm in Sweden from 18-20 May 2005. Approximately 250 persons were present during the conference.

The organizers state that the next generation of automotive fuels shall be:
- renewable and CO$_2$ neutral,
- available as a large global resource,
- energy efficient from well-to-wheel,
- cost-competitive with fossil fuels.

Thermal gasification of biomass fulfils these demands and is a key technology for producing second generation biofuels. Appendix A contains the complete conference programme. Presentations are available via www.ecotraffic.se/synbios.

1.3 Biofuels

First generation biofuels are presently on the market and comprise PPO (pure plant oil), FAME (fatty acid methyl esters like RME: rape seed methyl ester), biogas, and ethanol from starch and sugar. Second (and third) generation biofuels are generally characterised by a better environmental performance and a higher front-end flexibility than first generation biofuels. Second generation biofuels are Fischer-Tropsch fuels, DME, methanol, ethanol from lignocellulosic feedstocks like wood and straw, mixed alcohols produced from synthesis gas, Substitute Natural Gas (SNG), and H$_2$ (also sometimes referred to as third generation fuel).

In Figure 1.1, the main biofuels are ordered in a biomass versus generation matrix. Indicated are the categories of biofuels that need synthesis gas (a mixture of H$_2$ and CO) as intermediate product. It is clear that second (third) generation biofuels largely rely on synthesis gas. More detailed information on each biofuel can be found in [1].
### 1.4 Synthesis gas definition

In this report, synthesis gas or syngas is defined as a gas that contains H\(_2\) and CO as main combustible components. Raw syngas mostly inevitably contains also considerable amounts of CO\(_2\) and H\(_2\)O. Since syngas generally is used for the synthesis of chemicals and fuels (see Figure 1.1) at elevated pressures, the concentration of N\(_2\) in syngas usually should be minimised. Bio-syngas is chemically identical to syngas, but is produced from biomass. This definition is in-line with the definition used within the SYNBIOS-conference.

Syngas is chemically different from gases that normally are produced by low-temperature gasification processes such as fluidised bed reactors. For clarity, the gas produced by these kind of reactors is called “product gas” in this report. Product gas is defined as a combustible gas that contains H\(_2\) and CO, but also considerable amounts of hydrocarbons like methane. Product gas also inevitably contains CO\(_2\) and H\(_2\)O and often N\(_2\).

### 1.5 This report

This report describes the options to produce synthesis gas from biomass (bio-syngas), which is generally considered a key intermediate for the production of second generation biofuels. This report gives an overview of relevant items concerning bio-syngas in which information from the SYNBIOS-conference is added.
2. Syngas market

To date, syngas is an important intermediate product in chemical industry. Annually, a total of about 6 EJ of syngas is produced worldwide, corresponding to almost 2% of the present total worldwide primary energy consumption. The world market for syngas (mainly from fossil energy sources like coal, natural gas and oil/residues) is dominated by the ammonia industry. Other main applications are the production of hydrogen for use in refineries, e.g. hydrogenation steps, and for the production of methanol. Figure 2.1 shows the present syngas market distribution.

![Syngas market distribution](image)

**Figure 2.1. Present world syngas market, totally ~6 EJ/y [2].**

Today’s, global use of syngas for the production of transportation fuels in the so-called “gas-to-liquids” processes (GtL) correspond to approx. 500 PJ per year, i.e. from the Fischer-Tropsch processes of Sasol in South Africa and of Shell in Bintulu, Malaysia. In the future, syngas will become increasingly important for the production of cleaner fuels to comply with the stringent emission standards. Syngas is the intermediate energy carrier for the production of second generation biofuels like methanol, DME, cellulosic ethanol, and Fischer-Tropsch diesel. The huge potential market for syngas is illustrated by the fact that almost 20% of the present world primary energy consumption is for transportation fuels only [3]. If the chemical sector is included, the total global syngas potential increases to approximately 30%.

Biomass is heading for a great future as renewable energy source. It not only is available in large quantities, it also is the only renewable energy source that is suitable for the sustainable production of (generally carbon containing) transportation fuels and chemicals. Therefore, the application of biomass as feedstock for the production of fuels and chemicals allows the reduction of fossil fuel consumption and the accompanying CO₂-emmissions.

2.1 Scale

Ambitious national and international goals, like the biofuel directive of the European Union, call for large biosyngas production capacity. Not only are large installed capacities necessary, also the individual plants have to be large considering the typical plant scales for the two main applications today: several 1000 MWₜₕ for transportation fuels (e.g. Fischer-Tropsch and
methanol), and 50-200 MWth for the chemical sector. The large scale of existing plants is the result of the huge market and the dominant effect of economy-of-scale. This is expected to be not different from the situation that will occur for biofuels in the future.

Illustratively, it can be calculated that every percent of biofuel in the transportation sector of the EU-25 countries requires 10 large plants of 1000 MWth biomass input capacity each.

### 2.2 Implementation of biosyngas

Several large biosyngas plants are required to meet the ambitious renewable synthesis gas energy targets [4]. This requires a robust, fuel-flexible, and high-efficient technology for optimum biomass utilisation and good availability. Two possible routes can be followed, see Figure 2.2.

The first route comprises up-scaling of the small and medium scale gasification technologies that are currently mostly used for distributed heat and power (CHP) production. In this route it will take a long time before a significant biosyngas production capacity is installed. Either, a large number of plants have to be put in operation or the technology has to be up-scaled, which will take an additional development period of a decade.

The second route comprises adapting today’s large-scale coal-based gasification technology. In this way the accumulated installed biosyngas capacity can be increased rapidly, as the basic technology is already proven on large scale. It needs to be realized that coal-fired IGCC power plants have become increasingly popular recently because of the option to have CO2 separation and storage. Recently, the Dutch utility company NUON announced plans to realize a multi-fuel 1200 MWth IGCC power plant in the Netherlands. Both CO2 separation (for clean coal power) and biomass co-gasification are mentioned explicitly [5].

![Figure 2.2. Roadmap for large-scale implementation of bio-syngas, two possible routes](image-url)
3. Biofuel strategy

3.1 Facts and goals

According to Eurostat, the total transportation sector in the EU25 countries is responsible for 20% of the primary energy consumption. This equals roughly 15,000 litre per second. EU directive 2003/30/EC has set targets of 2% biofuels by the end of 2005 and 5.75% in 2010. For 2020, 8% has been mentioned, but also 15% has been proposed by the EU Alternative Fuels Contact Group. The vision goal of the European Technology Platform Biofuels is 25% biofuels in 2030.

In 2003, 0.7% biofuels are implemented in the EU-25 countries in average [6]. The contribution of each country is shown in Figure 3.1. According to Raldow (European Commission) biofuels account for 0.5% (2003) in Europe [7], which is similar to the world’s average [8].

![Figure 3.1. Share of biofuels in the transportation sector in EU-25 countries in 2003 [6]](image)

If the national targets for 2005 of each country will be reached, 1.5% biofuels will be consumed by the end of 2005 [6]. Raldow shows that the current trend in Europe leads to approximately 3.5% in 2010, rather than the targeted 5.75%. Raldow continues by saying that the commission
proposed a doubling of the R&D budget of the 7th Framework Programme (2007-2013) compared to the 6th Framework Programme [7]. Furthermore, the concept of technology platforms is introduced. The platform will be industry driven and will develop an EU-vision and action plan.

Unlike most other European countries, Sweden will reach the European goal of 2% biofuels in the transport sector in 2005. Sweden has targeted for even 3% in 2005 and has created the right (economic) conditions [9]. Since 2004, all petrol in Sweden contains 5% ethanol [10]. The ethanol mainly originates from Brazil and from wine production sites in Southern-Europe. Only 20% of the ethanol is produced nationally. At present, ethanol (E85) can now be purchased at 160 fueling stations in Sweden.

The 5.75% EU-goal for 2010 will probably be adapted by the Swedish government. A base case scenario for 2010 is 2.8% ethanol (mainly blending), 2% RME blending, 0.7% biogas/CNG in cars and buses, and 0.2% from DME and methanol [11]. Approximately 70% of the biomass fuels should be imported. The Swedish plans to actually reach the 5.75% target are: obligation for fuel stations to sell at least one type of biofuel, 10% ethanol blending in petrol and 5% RME blending in diesel, and the introduction of a green certificates system for renewable fuels [11]. For the longer term, it is stressed that R&D must focus on second generation fuels. Three biofuel plants have now been realised in Sweden: ethanol pilot plant in Örnsköldsvik, biomass gasification centre in Värnamo, and black liquor gasification plant in Piteå. More details of these latter two plants can be found in Chapter 4.

3.2 Reasons

Ahlvik identifies three problems that justify the development of alternative fuels: emissions on the short term, climate in the medium term, and security of supply on the long term [12].

Aleklett focuses on the depletion of fossil oil reserves. As a member of ASPO (Association for the Study of Peak Oil and gas, www.peakoil.net), Aleklett stresses the fact that petroleum is a major driving force of the world economy, but it is only a temporarily energy source as illustrated in Figure 3.2. World oil production will soon reach its peak production. ASPO’s view is that we should anticipate now to have a smooth energy transition [13]. Although one might argue on the exact moment when the oil production will have its peak [14], it is generally accepted that it will happen soon and an energy transition is unavoidable.
According to Azar (Chalmers Göteborg University), biofuels should compete with fossil fuels in the coming decades, whereas the major competitor on the long term is hydrogen or fossil fuels with CO$_2$ capture [15]. Electric transport is considered too impractical and too costly to become a short term success and to compete with biofuels.

Volkswagen believes that the GtL world market volume will increase enormously the coming decade. Volkswagen’s fuel strategy mentions GtL/CtL as intermediate between the present situation and the BtL option, but also Volkswagen considers hydrogen in fuel cells as the long-term option for transportation applications [16].
4. Syngas production

There are two thermo-chemical ways to produce synthesis gas (H$_2$ and CO) from biomass: either by applying high temperatures or by using a catalyst at a much lower temperature [17]. The first route generally requires temperatures as high as 1300°C and generally involves an entrained flow gasifier. The second route includes a fluidised bed gasifier and a downstream catalytic reformer, both operating at approximately 900°C. The two options concern two different evolution trajectories. The following sections cover the two options.

4.1 Fluidised bed gasification plus catalytic reformer

Fluidised bed gasification of biomass presently is a common way of converting biomass. Many different technologies are available. The air-blown circulating fluidised bed (CFB) is the most common one. Most fluidised bed applications involve close-coupled combustion with little or no intermediate gas cleaning. Electricity and/or heat are the usual end products.

The gas produced by a fluidised bed gasifier (typically operated at 900°C) contains H$_2$, CO, CO$_2$, H$_2$O, and considerable amounts of hydrocarbons like CH$_4$, C$_2$H$_4$, benzene and tars. Although this so-called product gas is suitable for combustion processes, it does not meet the requirements of synthesis gas, which is needed to produce biofuels or chemicals. The product gas needs further treatment in a catalytic reformer where hydrocarbons are converted into H$_2$ and CO (and CO$_2$ and H$_2$O). Since most syngas conversion to liquid fuels requires raw gas with very little or no inert gases, gasification and reforming should apply pure oxygen instead of air. Steam is usually added as a moderator. Another option to avoid N$_2$ dilution is to use an allothermal or indirect gasifier. In these reactors, gas production and heat generation do not take place in the same reactor. This enables the use of air (in the heat generating reactor), without having the N$_2$-dilution of the gas coming from the gas generation reactor. Examples of indirect gasifiers are the SilvaGas-process developed by Battelle in the US [18], MTCI-process [19], FICFB-concept developed by the university of Vienna [20], and MILENA developed by ECN [21,22].

In the EU-funded project Chrisgas, the existing 18 MW$_{th}$ pressurised CFB-gasifier in Värnamo will be refurbished to produce syngas [23]. This includes operation on oxygen/steam instead of air, the installation of a high temperature filter, a catalytic reformer, and a shift reactor. In 5 years time, the plant should produce 3500 m$_3$/h H$_2$ and CO at 10 bar. The project is carried out by the VVBGC consortium (Växjö Värnamo Biomass Gasification Centre). In the next phase, fuel synthesis will be added to the plant.

Another initiative in this category is by VTT, that advocates fluidised bed gasification as the process to generate clean fuel gas as well as syngas from biomass. Fuel flexibility is considered the major advantage. VTT recently started the UCG-programme (Ultra Clean Fuel Gas) and a 500 kW$_{th}$ PDU is under construction [24]. It consists of a pressurised fluidised bed, catalytic reforming, and further cleaning and conditioning. The catalytic reformer is meant to reduce hydrocarbons (benzene and larger) completely and methane by over 95%. The test unit will support RD&D focusing on methanol and Fischer-Tropsch diesel production via syngas as well as the production of SNG, H$_2$, and electricity by fuel cells. The present estimate of a 300 MW$_{th}$ plant based on above-described VTT process show that Fischer-Tropsch diesel and methanol can be produced for approximately 12 €/GJ (feedstock price 2.8 €/GJ). A plant this size can be largely constructed as a single train.
The German institute CUTEC has recently constructed an oxygen-blown 0.4 MWth CFB gasifier connected to a catalytic reformer. Part of the gas is compressed and directed to a Fischer-Tropsch synthesis reactor [25].

Apart from the above-mentioned initiatives to develop technology to produce syngas by fluidised bed gasification and catalytic reforming, many others apply catalytic reforming reactors for gas conditioning. This however, generally focuses on the catalytic reduction of large hydrocarbon molecules (viz. tars). Reforming methane usually is not one of the goals in these concepts.

### 4.2 Entrained flow gasification

The non-catalytic production of syngas (H\textsubscript{2} and CO) from biomass generally requires high temperatures, typically 1300°C. The most common reactor for this is the entrained flow gasifier [26]. Since biomass contains mineral matter (ash), a slagging entrained flow gasifier seems to be the most appropriate technology [27].

Entrained flow reactors need very small fuel particles to have sufficient conversion. This requires extensive milling of solid fuels, which is energy intensive and generally produces particles that cannot be fed by conventional pneumatic systems [27]. R&D therefore focuses on ways to technically enable the fuel feeding as well as improve the economics of the whole chain. The most promising pre-treatment options are torrefaction and pyrolysis. These options enable efficient and cheap production of syngas from biomass, mainly because it is characterised by relatively cheap (long-distance) transport.

Different slagging entrained flow gasifiers are operated worldwide, but only few have experience with biomass. Future Energy in Freiberg in Germany commercialises entrained flow gasifier technology for biomass, waste, and other fuels [28]. It owns a 3 MWth pilot plant that has been operated with many different biomass fuels. Furthermore, Future Energy supplied the 120 MWth entrained flow gasifier, which is commercially operated on waste material in the Schwarze Pumpe in Germany [29]. Another example is the Buggenum IGCC-plant in the Netherlands where biomass is co-gasified with coal in a slagging entrained flow gasifier. Tests have been conducted using up to 34 wt% biomass in the mixture [30]. This biomass is mainly sewage sludge and chicken manure, which does not generate pulverizing problems and feeding problems when mixed with coal. Also a mixture of coal and wood dust has been tested successfully.

#### 4.2.1 Torrefaction

Torrefaction is a mild heat treatment at 250-300°C that efficiently turns solid biomass into a brittle, easy to pulverise material (“bio-coal”) that can be treated as coal [31,32]. Furthermore, torrefied biomass can be pelletised very easily to obtain a dense and easy to transport biomass fuel [33]. The hydrophobic nature of torrefied material further simplifies logistics. Pulverized torrefied biomass can be fed like coal, thus enabling a smooth transition from coal to biomass.

Although torrefaction is a rather common process in e.g. coffee industry, it has never been optimised for efficient production of a brittle “bio-coal”. Research at ECN shows that the conversion of wood into a torrefied wood with similar milling characteristics as hard coal can have a 90-95% LHV efficiency. The gases produced during torrefaction can be used to supply the thermal needs of the process.
4.2.2 Pyrolysis slurry

Pyrolysis takes place at approximately 500°C and can convert solid biomass into a liquid product (bio-oil) in a process that is called flash-pyrolysis. The conversion efficiency will increase to 90% by including char in the oil to produce a bio-slurry [34,35]. Slurries can be pressurized and fed relatively easily.

FZK developed a concept to produce syngas from agricultural waste streams like straw [35]. In this concept, straw is liquefied locally by flash pyrolysis into an oil/char slurry, which is subsequently transported and added to a large pressurized oxygen-blown entrained flow gasifier. This approach offers the advantage of low transport costs of the energy dense slurry and large-scale syngas production and synthesis. At the same time, the problem of pressurising biomass is solved, since slurries are pumpable. An important patented feature of the concept is formed by the fact that milling of char can turn a solid mass into a liquid slurry by eliminating the volume of the pores of the char [36].

Flash pyrolysis plants typically will be 100 MWth input capacity. FZK developed the Lurgi-Ruhrgas concept that includes twin screws for pyrolysis. A 5-10 kg/h PDU is available at the premises of FZK. Several slurries have been tested in the 500 kg/h entrained flow gasifier of Future Energy in Freiberg to study its gasification and slagging behaviour [37]. Slurries from straw have been successfully converted into syngas with high conversion and near zero methane content. Ultimately, a biomass-to-liquid plant can have efficiencies as shown in Figure 4.1. Final biofuel costs will be around 1 €/kg (approximately 23 €/GJ) if feedstock price is 3 €/GJ straw [35].

Figure 4.1. Energy flows in the FZK-concept where lingo-cellulose is pre-treated into a pyrolysis oil/char-slurry and subsequently converted in syngas and Fischer-Tropsch products [35]
4.2.3 Black liquor

Existing pulp and paper industry offers unique opportunities for the production of biofuels with syngas as intermediate. An important part of many pulp and paper plants is formed by the chemicals recovery cycle where black liquor is combusted in so-called Tomlinson boilers. Substituting the boiler by a gasification plant with additional biofuel and electricity production is very attractive, especially when the old boiler has to be replaced. The economic calculations are based on incremental costs rather than absolute costs. This method seems generally acceptable [38-41] and leads to e.g. methanol production costs of 0.3-0.4 €/litre of petrol equivalent [39-41]. It must be realised that biofuel plants, which are integrated in existing pulp and paper mills should match the scale of the paper mill. The integrated biofuel plant therefore is typically 300 MWth [40], which is at least 10 times smaller than commercial fossil fuel based methanol and Fischer-Tropsch plants.

Efficiencies of biofuel plants, which are integrated in pulp- and paper industry, are often reported based on additional biomass, which is needed to produce the additional biofuels. This results in very high reported values of 65% to even 75% [40,41].

Chemrec develops a technology needed to convert black liquor into syngas to subsequently produce biofuels like DME, methanol, etc. [40]. It is a dedicated entrained flow gasifier operated at temperatures as low as 1000-1100°C. This is possible due to the presence of large amount of sodium, which acts as a gas-phase catalyst in the gasifier. Chemrec constructed DP1, a 3 MWth entrained flow gasifier operating at 30 bar in Piteå in Sweden next to the Kappa paper mill, see Figure 4.2. It includes gas cooling by water quench and gas cooler. The syngas will have a composition (vol% dry) of approximately: 39% H₂, 38% CO, 19% CO₂, 1.3% CH₄, 1.9% H₂S, and 0.2% N₂. At present, the pilot plant is being commissioned. Demonstration plant DP2 will be a black liquor gasification combined cycle (BLGCC) plant in Piteå. DP3 will be located in Mörrum. This will produce a biofuel. Both plants will be constructed in 2006/2007.

Figure 4.2. Chemrec black liquor gasification demonstration plant [40]
Implementation of such concept in the US paper and pulp industry could produce 4.4% of current US petroleum/diesel consumption\(^1\) [38]. In Finland and Sweden this could be significant, as high as 51% and 29% of the respective national use of transportation fuels [41].

4.2.4 Choren

Choren develops the Carbo-V concept where solid biomass is pre-treated by slow pyrolysis to yield char and gases [42]. The gases are gasified at high temperature (typically 1300°C) to generate syngas. The char is pulverized and injected downstream the high-temperature reactor in order to cool the syngas by endothermic char gasification reactions. This so-called chemical quench cools the syngas to approximately 1000°C. The concept has been demonstrated in the 1 MW\(_{th}\) \textit{alpha} plant in Freiberg. Since 2003, biofuel synthesis has been added to the plant. After a short period of methanol synthesis, the unit was modified to Fischer-Tropsch synthesis. The Fischer-Tropsch diesel is called sundiesel.

Late 2002, Choren started the construction of the 45 MW\(_{th}\) 5 bar \textit{beta} plant in Freiberg. Early 2007, this plant is projected to produce sundiesel with approximately 50% thermal efficiency from wood.

4.3 Polygeneration

The previous sections focused on the production of syngas with high yields of H\(_2\) and CO. This is desirable in order to get the maximum production efficiency of biofuels/chemicals like methanol and Fischer-Tropsch diesel. The alternative approach is called polygeneration. In this case, the H\(_2\) and CO from a gas are used for the (once-through) synthesis of a biofuel/chemical and the remaining components in the gas are used in a different way, e.g. de production of electricity.

The waste gasification plant of the Schwarze Pumpe in Germany is an example where waste is converted into a product gas containing considerable amounts of hydrocarbons. The gas is cleaned and used as feedstock to produce methanol. The remaining gas (mainly methane) is used as fuel for a 75 MW\(_e\) combined cycle to produce electricity [29,43].

4.4 Biorefinery

Another integrated biofuel concept is sometimes referred to as biorefinery. A concept that is of great interest in the US is where conventional (biological) fermentation is combined with thermo-chemical conversion with syngas as intermediate product. This concept efficiently produces ethanol and other alcohols from different kinds of biomass. This so-called advanced ethanol refinery plant is expected to produce alcohols for less than 1 $/gallon (approximately 10 €/GJ) [44].

\(^1\) At the same time, 4.6% of the current coal-electricity would be replaced by renewable energy.
5. Syngas conditioning

In the previous chapter, main gasification technologies have been presented for the production of syngas from biomass. Generally, technologies were selected for their high efficiency to produce H$_2$ and CO, with little or no hydrocarbons. The presence of minor impurities like sulphur, chlorine, ammonia, and soot will however be inevitable. Since the concentration of these components generally exceed the specification of a catalytic synthesis reactor (methanol, Fischer-Tropsch, …), gas cleaning is necessary. Table 5.1 shows indicative syngas specifications that have been adapted from Fischer-Tropsch and methanol catalysis processes. It must be realized that there is an economic trade off between gas cleaning and catalyst performance. Cleaning well below the specifications as mentioned below, might be economically attractive for synthesis processes that use sensitive and expensive catalytic materials.

Table 5.1. Maximum allowable concentration of impurities in syngas [45]

<table>
<thead>
<tr>
<th>impurity</th>
<th>specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S + COS + CS$_2$</td>
<td>&lt; 1 ppmv</td>
</tr>
<tr>
<td>NH$_3$ + HCN</td>
<td>&lt; 1 ppmv</td>
</tr>
<tr>
<td>HCl + HBr + HF</td>
<td>&lt; 10 ppbv</td>
</tr>
<tr>
<td>alkali metals (Na + K)</td>
<td>&lt; 10 ppbv</td>
</tr>
<tr>
<td>particles (soot, ash)</td>
<td>“almost completely removed”</td>
</tr>
<tr>
<td>organic components (viz. tar)</td>
<td>not condensing: below dew point</td>
</tr>
<tr>
<td>hetero-organic components (incl. S, N, O)</td>
<td>&lt; 1 ppmv</td>
</tr>
</tbody>
</table>

Since raw bio-syngas resembles syngases produced from more conventional fuels like coal and oil residues, gas cleaning technologies will be very similar. This means that it most probably will include a filter, Rectisol unit, and downstream gas polishing to remove the traces. This involves e.g. ZnO and active carbon filtering. Because the H$_2$/CO-ratio generally needs adjustment, a water-gas-shift reactor will also be part of gas conditioning. The Rectisol unit then combines the removal of the bulk of the impurities and the separation of CO$_2$.
6. Biofuels from syngas

6.1 Synthesis

A cleaned and conditioned bio-syngas can be used for the synthesis of many products such as biofuels. In Figure 1.1, the most popular second generation biofuels have been mentioned: Fischer-Tropsch diesel and other oil products, methanol, dimethyl-ether (DME), mixed alcohols (MA), and even pure H₂.

The production efficiency depends on the type of biofuel. Theoretically, the LHV efficiency with natural gas as feedstock is 84%, 82% and 78% for methanol, DME and Fischer-Tropsch diesel respectively. The actual LHV efficiencies are lower: 68%, 71% and 63% respectively [46]. In Japan, JFE reached 69% DME production efficiency from natural gas in the 100 ton/day (~20 MWth) slurry phase DME reactor demonstration plant in Kushiro [47].

In principle, biofuels production is not different from processes where fossil syngas is used. There are however a few biomass-related items that might change the concept. One of those already mentioned is the scale of operation. Whereas fossil based syngas plants typically are huge, some believe that biomass plants may not be larger than several 100 MWth, the size of a typical paper and pulp mill. The limiting factor could be the availability of biomass feedstock at a negotiated price. Downscaling the size might lead to different biofuel synthesis concepts.

Another difference between biofuels synthesis and the conventional processes for the production of products and chemicals from syngas relates to process integration. Section 4.1 already mentioned the option to combine chemical recovery and biofuel synthesis in a paper and pulp mill by the gasification of black liquor. Another option that might change the concept is the possibility to recycle by-products. This is mentioned by Choren, where naphtha produced in the Fischer-Tropsch synthesis is recycled to the gasifier to increase the efficiency of the diesel production [48].

A completely different way of increasing the renewable character of transportation fuels is to add H₂ from biomass in a refinery as green substitute for H₂ made by reforming natural gas or residues. Although this option is limited in volume, it is relatively cheap because it does not involve biofuel synthesis and upgrading. Instead, clean syngas will suffice. Legislation and calculation methods however need to be adapted to this alternative “biofuel” option.

6.2 Substitute Natural Gas

Substitute Natural Gas (SNG) from biomass can be considered a biofuel. SNG contains mainly methane and resembles natural gas. It can be synthesised from syngas, but this is not very efficient. Better efficiencies can be obtained with “product gas”, already containing significant amounts of methane. This generally means that gasification should take place non-catalytically at around 900°C. At these temperatures, methane destruction generally is limited because of kinetic reasons. Fluidised bed gasification is one of the obvious options.

The production of SNG from biomass therefore requires a totally different approach than the production of biofuels through syngas. It is quite possible that gasification technologies, gas cleaning and upgrading technologies could be very different. For example tars play a crucial role in SNG synthesis. R&D on SNG from biomass is concentrated at PSI [49,50] and ECN [22,51,52].
6.3 Biofuel applications

Volvo focuses on DME as biofuel for transport because it has the highest well-to-wheel energy efficiencies and lowest CO\textsubscript{2}-emissions of all biofuels (see Figure 6.1). Furthermore, DME results in zero particle matter in flue gases and is a multi-source and multi-purpose fuel.

![Figure 6.1. Well-to-wheel performance for different fuels [53]](image)

Volvo started research into DME 10 years ago. Figure 6.2 shows the first Volvo FM9 300 hp truck running on DME. It meets the new Euro-5 standards. The coming years, Volvo will produce 3 trucks to perform a field test starting January 2007 [54].

![Figure 6.2. Volvo truck running on DME [54]](image)
Volkswagen focuses on Fischer-Tropsch diesel as the second generation biofuel. It is called “sunfuel” or “sundiesel” [16]. This is chemically identical to Fischer-Tropsch diesel (“synfuel”) made from gas (GtL) or coal (CtL). Fleet tests performed by Volkswagen with Fischer-Tropsch diesel show significant improvements compared to conventional low-sulphur fossil diesel. CO and hydrocarbon emissions reduced by 91% and 63%. The emission of particulates reduced by 26% and even NO\textsubscript{x} was reduced by 6% [55]. These improvements add up to the original CO\textsubscript{2}-emission reduction argument to use biomass-based Fischer-Tropsch diesel (sunfuel). Renault has also performed tests where the reduction of soot emissions was shown when Fischer-Tropsch diesel was used compared to fossil diesel [55].
7. Concluding remarks

Making \( \text{H}_2 \) and CO (syngas) from biomass is widely recognised as a necessary step in the production of second generation biofuels. The first step is to convert biomass into a syngas. There are two major approaches:

- Fluidised bed gasification: biomass is converted to fuel gas at approximately 900°C. This option requires almost no biomass pre-treatment, but the product gas needs downstream catalytic upgrading. A catalytic reactor is needed to reform the hydrocarbons to syngas. Support R&D is being performed at VTT (Finland), Värnamo (Sweden), and CUTEC (Germany). The fluidised bed gasification approach has the advantage that the gasification technology has been developed and already demonstrated with biomass for the production of heat and/or electricity.

- Entrained flow gasification: fuel is converted at high temperature into a syngas with little or no methane and other hydrocarbons. It generally requires 1300°C, but it can be as low as 1000-1100°C if the biomass has sufficient catalytically active components like K or Na, which is the case for e.g. straw and black liquor. Most biomass feedstocks are not suitable to be directly injected into an entrained flow gasifier because the fuel size needs to be small. Extensive pre-treatment is therefore required. There are different ways to deal with this:
  - Flash pyrolysis: biomass is converted at approximately 500°C into a liquid oil/char-slurry, which can be atomised in an entrained flow gasifier. Another attractive aspect is that the high-energy density slurry can be transported to a central processing facility. This generates an economic gain to this concept. FZK in Germany is focusing on this option in cooperation with Future Energy.
  - Slow pyrolysis: biomass is converted at approximately 500°C into a char. The char is pulverised and directed to the entrained flow gasifier. Since the pyrolysis also produces an excess of gas, the gas needs to be utilized efficiently. Choren (Germany) follows this route and added an important item to the concept: the char is injected into the high-temperature syngas in order to cool it by endothermic heterogeneous gasification reactions. The Choren-approach is characterised by high efficiency, but the direct coupling of pyrolysis and entrained flow gasification excludes the option to transport the intermediate product.
  - Torrefaction: biomass is thermally treated at 250-300°C to produce a brittle and easy to pulverize fuel. This can be done on the site, but also before transporting the solid fuel. The latter is attractive since torrefied biomass not only pulverizes easily, but also subsequent pelletisation consumes relatively little energy. The torrefied biomass pellet has a high energy density and thus offers economic gains in transport. ECN in the Netherlands pursues the torrefaction pre-treatment option.
  - Fluidized bed gasification: biomass is converted at 600-900°C into a gaseous intermediate, the so-called product gas, with significant amounts of small char particles entrained with it. The mixture is directed to the high temperature entrained flow gasifier to convert it to syngas. This combination has a very high efficiency and allows the feeding of conventional chips. The connection between the two gasifiers however, is less conventional.

The entrained flow gasification processes have already been developed and demonstrated on large-scale for coal. In some cases even mixtures of coal and biomass have been tested successfully.

It should be realised that the above-mentioned options are not necessarily competing processes. The preference very much depends on boundary conditions, based on fuel type and fuel
availability. Optional process schemes could be developed integrating these concepts to produce bio-syngas\(^2\).

Bio-syngas can be used to synthesize different types of biofuels such as Fischer-Tropsch fuels, methanol, DME, mixed alcohols, and even pure hydrogen. However, extensive syngas cleaning and conditioning is required in all these applications. Figure 7.1 shows the above-described options to produce biofuels from biomass.

Figure 7.1. Different pathways from biomass to biofuels with syngas as intermediate

The scale of the plants is an important issue. The back-end of the process generally needs to be as large as possible because of the dominant economy-of-scale effect in biofuel synthesis and upgrading. The front-end however involves biomass supply. This generally means that increasing plant size means higher feedstock costs because longer transport distances are involved\(^3\). There is however an attractive way to deal with this scale “mismatch” by splitting the two parts: biomass is pre-treated in relatively small-scale plants close to the geographical origin of the biomass and the intermediate is transported to a central large-scale plant where it is converted into a biofuel. The pre-treatment should preferably result in an easy to transport material. Conventional pelletisation is an option, but more attractive is the use of dedicated pre-treatment that also produce a feedstock that can be used directly in the large-scale syngas plant. This might be the production of an oil/char slurry by fast pyrolysis or the production of torrefied wood pellets.

\(^2\) The integration options include the integration with the chemical cycle in pulp- and paper industry, but can also include fuel upgrading or heat users.

\(^3\) Note that existing pulp and paper mills typically have 400-600 MW\(_{th}\) biomass input capacity, biomass supply logistics being one of the main limiting factors.
8. References


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33. P. C. A. Bergman: Combined torrefaction and pelletisation, the TOP process, ECN, Petten, the Netherlands, 29 p. (2005).


47. M. Omiya: Development of DME direct synthesis process, demo plant and project results of biomass gasification to DME. In: Synbios, the syngas route to automotive biofuels, conference held from 18-20 May 2005, Stockholm, Sweden (2005).


55. F. Seyfried: *Tomorrow's fuels for advanced power trains, engine test emission results.*

In: Synbios, the syngas route to automotive biofuels, conference held from 18-20 May 2005, Stockholm, Sweden (2005).
Appendix A  SYNBIOS conference programme

The SYNBIOS conference was held in Stockholm in Sweden from 18-20 May 2005.

| Session: Political Strategies & Visions | Chair: Dr. Tomas Kåberger
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<td>Mr. Thomas Korsfeldt, Director General, Swedish Energy Agency</td>
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<td>Dr. Kjell Aleklett, President, Association for the Study of Peak Oil</td>
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<td>Dr. Wiktor Raldow, Head of Unit Directorate J, DG Research, European Commission</td>
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<td>Market and potential for wood fuel, vision and strategy for the forest industry</td>
<td>Dr. Erik Ling, Market Manager, Biofuel, Sveaskog</td>
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<td>Stabilising the world’s carbon dioxide emissions, the need for measures beyond the Kyoto treaty</td>
<td>Dr. Christian Azar, Professor, Physical Resource Theory, Chalmers</td>
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<td>Dr. André Faaij, Professor, Dept. Science, Tech., Utrecht University</td>
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<td>Mr. Henrik Landålv, Manager, Environmental Projects, Volvo Powertrain Corp.</td>
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<td>Biomass-based synthetic fuels as an integral part of Volkswagen's fuel strategy and the RENEW project</td>
<td>Dr. Frank Seyfried, Head of Group Research, Fuels &amp; Oils, Volkswagen</td>
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### Session: Research & Market

**Chair: Dr. Tomas Kåberger**

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<td><strong>Mr. Hans Sandebring</strong> Ex-Commissioner Ministry of Environment</td>
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<td>Syngas routes to alternative fuels, efficiencies and potential with update on current projects</td>
<td><strong>Dr. John Bøgild Hansen</strong> Senior Scientist Haldor Topsøe</td>
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<td>Development of DME direct synthesis process, demo plant and project results of biomass gasification to DME</td>
<td><strong>Mr. Mamoru Omiya</strong> Manager of Catalyst Developm. Team JFE Holdings</td>
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<td>Techno-economics of biomass &amp; black liquor gasification for automotive fuel production</td>
<td><strong>Mr. Tomas Ekbom</strong> Technical Director Nykomb Synergetics</td>
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### Parallel session: Thermo-Chemical Conversion

**Chair: Dr. Suresh P. Babu**
**Gas Technology Institute**
**Chair: Ms. Eva K. Larsson**
**TPS Termiska Processer**

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<td><strong>Mr. Erik Rensfelt</strong> Consultant ERen Energy</td>
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<td>Novel ultra-clean concepts of biomass gasification for liquid fuels</td>
<td><strong>Mr. Esa Kurkela</strong> Group manager VTT Processes</td>
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<td><strong>Mr. Ingvar Landälv</strong> Technical Director Chemrec</td>
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<td><strong>Mr. Matthias Rudloff</strong> Head of Developm. Choren</td>
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### Parallel session: Vehicle Development and Fuel Market

**Dr. Tomas Kåberger**

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<td>Views on automotive fuels, current &amp; future regulations and emissions</td>
<td><strong>Mr. Olle Hådell</strong> Expert Swedish Road Administration</td>
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Tomorrow’s fuels for advanced power trains, engine test emission results

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Status of Neste’s biobased NExBTL-diesel production for 2007

Overview on novel and alternative fuels with strategies and visions

Synthetic BioDiesel: a step towards even more environmentally friendly vehicles

**Session: summaries**

Summary and highlights of session thermochemical conversion presentations

Summary and highlights of session vehicle development and fuel market presentations

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