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SYNTHESIS GAS FROM AGRICULTURAL FEEDSTOCK – A REVIEW OF POSSIBLE TECHNICAL PATHWAYS

Report from an f3 project

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THE SWEDISH KNOWLEDGE CENTRE
FOR RENEWABLE TRANSPORTATION FUELS

PREFACE

This project was carried out as a synthesis project by the Swedish University of Agricultural Sciences, within the f3 consortium. The f3-synthesis projects are more limited in time, scope and focus than full research projects. They usually describe a field of research, geographic region, or state of art for any biofuel-related activity, or consist of a literature review with e.g. comparative approach. Serina Ahlgren was the project leader in this project. Sven Bernesson conducted most of the literature search and writing.

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SUMMARY

Syngas, or synthesis gas, is a fuel gas mixture consisting of CO + H_2 in different proportions. In some cases, CO_2 is also included in the mix. Syngas is an important feedstock when producing many chemical products (e.g. ammonia and methanol), but also gaseous biofuels (e.g. substitute natural gas (SNG) and hydrogen) and liquid biofuels (e.g. Fischer-Tropsch diesel (FTD) and dimethyl ether (DME)). Syngas can also be used in turbines for efficient production of electricity and heat.

Much attention has been given to the possibility of thermal gasification of forest products, but there are other alternatives for syngas production. This report reviews the possibilities of converting agricultural feedstock (crops, manure, residues etc.) to syngas via (1) upgrading of biogas from anaerobic digestion and (2) thermochemical conversion. The focus of the review is on technical conversion systems rather than feedstock and it is based on existing literature, but we also present a rough energy analysis, examining some of the energy inputs and outputs to the system.

According to the literature, there are many different reforming techniques for production of syngas from biogas. The energy analysis indicated that the output energy (as H_2, CO and CH_4) from the reforming processes was largest from combined steam and carbon dioxide reforming. However, this process also requires high energy inputs due to very endothermic reactions in the reforming phase. If incoming methane is included in the calculations, the energy balance of the different types of reforming methods was very similar. The study also shows that energy for reforming dominate the process energy input, while energy use for upgrading biogas, desulphurisation and production of pure oxygen had marginal effects on net energy yield.

It was difficult to find a consistent method to compare energy balance between gasification and the anaerobic-to-syngas route. However, the anaerobic-to-syngas production route appears to be within the lower range of energy yields reported for gasification. Note that the energy analysis in this report is only indicative. Note also that anaerobic digestion and gasification should not be seen as competing but as complementary technologies, providing the opportunity for a diversity of raw material to be used as feedstock for syngas production.

When evaluating the different technologies scalability and costs are vital, and would be a logical continuation to this project. Another interesting follow-up project would be a more detailed study of energy balances and greenhouse gases for the different technical pathways, where the whole life cycle, including cultivation of feedstock, is included. Extending the system boundaries to include production of biofuels would be also interesting, as it would enable comparison with other types of biofuels. Further research on the technical side could also include studies on the development of small-scale reforming for biogas applications, as well as novel technologies such as plasma reforming.

SAMMANFATTNING

Syntesgas (eller syngas) är en gasblandning bestående av CO och H_2 i olika proportioner, ibland ingår även CO_2. Syntesgas är en viktig råvara vid tillverkning av många kemiska produkter (t.ex. ammoniak och metanol) men också för tillverkningen av gasformiga biobränslen (t.ex. Bio-SNG (SNG står för eng. substitute natural gas) och vätgas) och flytande biobränslen (t.ex. Fischer-Tropsch diesel (FTD) och dimetyleter (DME)). Syntesgasen kan även användas i gasturbiner för produktion av el och värme.

Mycket uppmärksamhet har hittills ägnats åt möjligheterna för syntesgasproduktion via termisk förgasning av skogsprodukter, men det finns även andra alternativa tekniker och råvaror för syntesgasproduktion. Syftet med denna rapport är att ge en översikt över möjligheterna att omvandla jordbruksråvara (grödor, gödsel, restprodukter etc.) till syntesgas via (1) uppgradering av biogas från rötning och (2) termokemisk förgasning med mer fokus på de tekniska omvandlingssystemen, och mindre fokus på råvarorna. Genomgången är baserad på litteratursökningar. Vidare utfördes en energianalys, utifrån vilken några av flödena av energi till och från systemet diskuteras.

Rapporten visar att det finns flera olika möjliga reformeringstekniker för produktion av syntesgas från biogas. Energianalysen visade att utgående energi (som H_2, CO och CH_4) från reformering var störst från systemet med kombinerad ång- och koldioxidreformering, men denna teknik kräver också en hög energiinsats då det är frågan om endoterma reaktioner i reformeringen. Om ingående metan inkluderas i energiberäkningarna, var energibalansen av väldigt lika storlek för de olika typerna av reformeringsmetoder. Studien visar också att energi för reformering dominerar i energiinsatserna, medan energianvändning för uppgradering av biogas, avsvavling och produktion av syrgas var av mindre betydelse.

Det var svårt att hitta en enhetlig metod för att jämföra energibalanserna mellan förgasning och rötning-till-syntesgas. Dock verkar det som om rötning-till-syntesgas ligger inom det lägre området för energibalanser som rapporterats för förgasning. Det bör dock noteras att energianalysen i den här rapporten endast kan ses som vägledande, då det är frågan om grova uppskattningar. Viktigt är också att rötning och förgasning inte bör ses som konkurrerande tekniker, utan snarare som komplementära, då de tillsammans ger möjlighet till en mångfald av råmaterial för produktion av syntesgas.

Vid bedömningen av de olika teknikerna är skalbarhet och kostnader avgörande, och det skulle vara en logisk fortsättning på detta projekt att studera dessa faktorer närmare. En annan intressant fortsättning på detta projekt skulle vara en mer detaljerad studie av energibalanser och växthusgaser för de olika tekniska lösningarna, där hela livscykeln inklusive odling av råvara ingår. Även en utvidgning av systemgränsen till att omfatta produktion av biodrivmedel skulle vara intressant, för att möjliggöra jämförelser med andra typer av biodrivmedel. Ytterligare teknisk forskning skulle kunna inkludera utvecklingen småskalig reformering för biogasapplikationer, samt ny teknik såsom plasmareformering.

CONTENTS

INTRODUCTION

Syngas, or synthesis gas, is a fuel gas mixture consisting of carbon monoxide (CO) and hydrogen gas (H_2) in different proportions. In some cases, carbon dioxide (CO_2) is also included in the mix. Syngas is an important feedstock when producing many chemical products (e.g. ammonia and methanol), but also gaseous biofuels (e.g. substitute natural gas (SNG) and hydrogen) and liquid biofuels (e.g. Fischer-Tropsch diesel (FTD) and dimethyl ether (DME)). Syngas can also be used in turbines for efficient production of electricity and heat. The desired ratio of H_2 to CO depends on the intended use of the syngas (Table 1).

Table 1. Desired H_2:CO ratio for different processes (Eliseev, 2009)

Process	H_2:CO
Ammonia production (maximum yield of hydrogen)	1:1
Methanol synthesis	2:1
Hydrocarbon synthesis	1.5: 1 or slightly lower

The feedstock used for syngas production varies, but fossil fuels currently dominate (Figure 1). Thermochemical gasification and pyrolysis of biomass has been proposed as a promising alternative for production of syngas, because of the large potential and the option of advanced applications. However, a review of the development of biomass gasification projects by Kirkels and Verbong (2011) showed that biomass gasification is not yet mature enough to be widely applied on the market, which is also reflected in Figure 1. It is still in a state of flux, there is no dominant design and in most markets it is unable to compete with other technologies. Kirkels and Verbong (2011) did not expect a breakthrough in the short term, with gradual niche development seeming much more likely. Others are more optimistic about the future of biomass gasification. A recent survey of experts in biomass gasification revealed that they are convinced that biomass gasification will be applied at large scale as soon as policy measures ensuring economic viability of the projects have been adopted (Heyne et al., 2013).

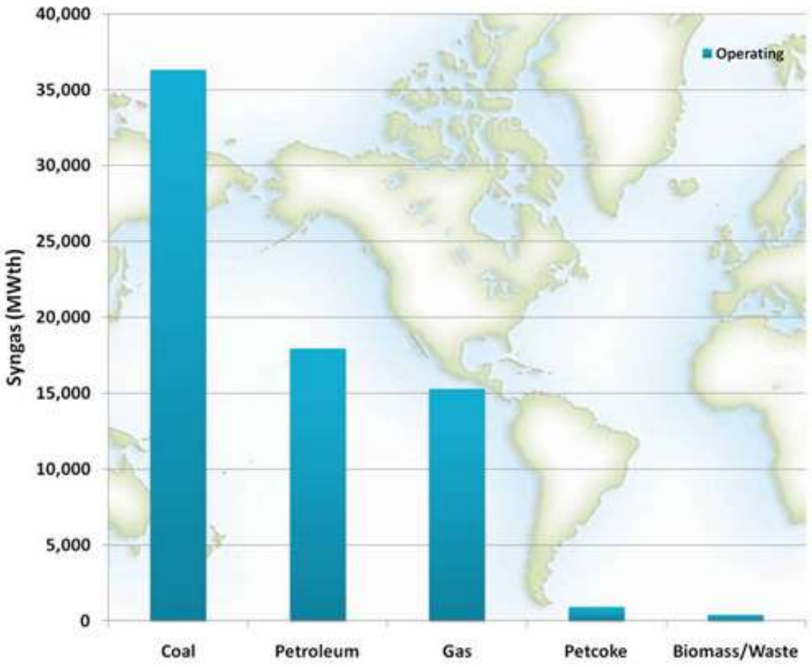

Figure 1. World syngas operating capacity by feedstock (NTEL DOE, 2010).

However, there are also other alternatives for syngas production. One interesting route would be to use biogas from anaerobic digestion (see e.g. Kolbitsch et al., 2008; Izquierdo et al., 2012). This technology would also open the way for utilisation of other types of biomass feedstock for syngas production. For anaerobic digestion, agricultural products, wastes, residues and manure are possible substrates, as well as waste from households and industry and sewage sludge. Different types of organic raw material (substrates) are suitable for different types of anaerobic digestion processes (e.g. dry or wet, thermophilic or mesophilic, batch or continuous, small or large scale) and give different methane yields. When evaluating substrates as feed for anaerobic digestion, several different aspects need to be taken into consideration, such as anaerobic degradability, total solids content (TS), volatile solids content (VS), nutrient composition and the risk of causing mechanical problems (Carlsson & Uldal, 2009).

The aim of this report was to review the possibilities of converting agricultural feedstock (crops, manure, residues etc.) to syngas via upgrading biogas from anaerobic digestion and thermochemical gasification. The main focus in the report was on technical conversion systems rather than the feedstock. The assessment was based on data obtained in literature searches. We also performed an energy analysis, to examine some of the energy inputs and outputs to the system.

FROM ANAEROBIC DIGESTION TO SYNGAS

Anaerobic digestion is a series of processes by which microorganisms break down biodegradable material in the absence of oxygen. The process produces raw biogas, which can be used directly as fuel in combined heat and power gas engines, or upgraded to natural gas-quality biomethane. The nutrient-rich digestate produced as a by-product can be used as a fertiliser.

This chapter reviews different technological pathways for producing syngas from raw biogas. Sulphur removal technologies are described first, since this is a vital step in syngas production. It may also be necessary to remove many other contaminants in the raw biogas, e.g. water vapour, NH_3, particles, siloxanes, oxygen, halogenated hydrocarbons and nitrogen. The presence of contaminants in the biogas is often dependent on the feedstock used in the anaerobic digestion process. For example, landfill gas can be expected to contain more contaminants than gas from digestion of e.g. manure. Biogas also contains chlorocarbons, which are potential catalytic toxins. Chlorocarbons are unique to biogas and bio-derived fuels due to the natural presence in organic material of chlorinated compounds, which are released during decomposition or thermal treatment (Kohn, 2012). The scope of this report did not allow us to examine all these contaminants in detail. For further reading on biogas cleaning, see e.g. López et al. (2012). Here we instead opted to focus on sulphur, which is one of the more crucial and commonly occurring elements that needs to be removed from raw biogas.

The next sections provide a description of different upgrading technologies, starting with removal of carbon dioxide, followed by a description of different reforming technologies to produce syngas. A key issue in reforming biogas is choice of catalyst, a decision which needs to consider both performance and cost. A brief discussion on catalysts is therefore also included.

Figure 2 provides an overview of the entire value chain and of the upgrading technologies studied in this report.

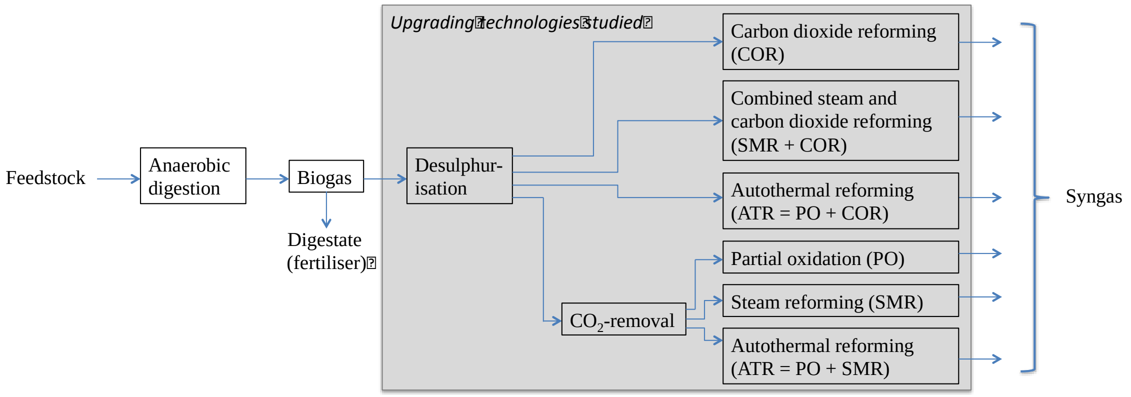

Figure 2. Overview of the value chain from anaerobic digestion to syngas, and specification of the upgrading technologies studied in this report (grey box).

1.1 REMOVAL OF SULPHUR

The raw biogas from anaerobic digestion mainly consists of methane (CH_4) and carbon dioxide. However, there are also a number of trace gases, among which sulphur (S) in particular is troublesome and needs to be removed before treating the gas further. Sulphur originates from the substrate and is formed when the substrate is degraded. An important characteristic of the substrate for prediction of sulphur production in the gas is the carbon:sulphur ratio (Peu et al., 2012).

Hydrogen sulphide (H_2S) in the biogas is corrosive to metals, causes wear when handling the gas and forms sulphur dioxide (SO_2) when combusted. The hydrogen sulphide content of biogas can vary in the range 10-10,000 ppmv. It converts to highly corrosive and environmentally hazardous sulphur dioxide and sulphuric acid (H_2SO_4) (Mota et al., 2011). It also has a foul odour. It is therefore important that the hydrogen sulphide is separated out as early as possible in the process. Several techniques exist to remove sulphur from the gas.

1.1.1 Biological desulphurisation - oxidation in the anaerobic digester or in biological scrubbers

A commonly used sulphur separation technique is to supply air to the anaerobic digester reactor so that an oxygen content of 2-6% is obtained, which causes bacteria that are naturally found in the organic material to precipitate sulphur on the digester walls and other equipment surfaces (Ryckebosch et al., 2011; Blom et al., 2012). The sulphur then finally ends up in the residue. This natural oxidation process is performed by bacteria of the genera Thiobacillus and Sulfolobus (Persson et al., 2006; TU Wien, 2012a, 2012b).

Another option for oxidation in the anaerobic digester is to let the gas leaving the digester pass through an external device (Persson et al., 2006; Ryckebosch et al., 2011; TU Wien, 2012a, 2012b). This consists of a trickling filter with a packed bed inside, in which the microorganisms form a biological slime. The raw biogas is mixed with the added air or oxygen, enters the trickling filter and there meets a counterflow of water-containing nutrients. The microorganisms oxidise any hydrogen sulphide present using oxygen and convert it into water and elemental sulphur or sulphurous acid, substances discharged with the wastewater from the column. The method requires moderate investment, has low operating costs and has high plant availability.

An advantage with biological desulphurisation is that use of chemicals can be avoided. The biological system can isolate large quantities of sulphur, but has significantly low ability to adapt to fluctuations in the content of hydrogen sulphide in the biogas. Therefore, the method is not suitable if fast fluctuations in the content of hydrogen sulphide in biogas from the anaerobic digestion plant can be expected. This means in practice that the method is only suitable for processes with a low or moderate hydrogen sulphide content in the biogas and where the substrates are not frequently changed. The method can also be used as a first step in sulphur removal, combined with other techniques.

1.1.2 Process internal desulphurisation - precipitation of sulphur with metal salts

Adding a liquid mixture of metal salts (e.g. iron chloride or iron sulphate) to the anaerobic digester results in the sulphur forming almost insoluble iron sulphide (Persson et al., 2006; Ryckebosch et al., 2011; TU Wien, 2012a, 2012b). The iron sulphide can then be removed from the digester together with the digestate. This method also has other advantages, e.g. it can reduce the amount of toxic substances (e.g. ammonia), which in turn may increase the methane yield, and it is relatively inexpensive, with almost no investment needs. Its disadvantages include difficulty in controlling the degree of desulphurisation, the impossibility of pro-active measures and clear limitations in the effectiveness and degree of purification that can be achieved. The method is suitable when the content of sulphur in the raw biogas is medium or high and can be applied as a subsequent step before final desulphurisation.

1.1.3 Chemical oxidative scrubbing

Raw biogas can be cleaned of hydrogen sulphide in a separate scrubbing step, by absorption of the hydrogen sulphide in a caustic solution consisting of e.g. sodium oxide (Ryckebosch et al., 2011; TU Wien, 2012a, 2012b). It is important to have precise control of the pH so as to adjust the separation selectivity and achieve high absorption of hydrogen sulphide and as low absorption of carbon dioxide as possible, in order to minimise the consumption of chemicals (carbon dioxide can be removed by other, more efficient technologies). The selectivity for hydrogen sulphide can be further increased by the application of an oxidising agent that oxidises the absorbed hydrogen sulphide to elemental sulphur or sulphate. The rate of desulphurisation increases accordingly. A commonly used oxidant in biogas plants is hydrogen peroxide. It is possible to reach stable operation at hydrogen sulphide contents of as low as 5 ppm, but the most economic operation is to control the purified gas at around 50 ppm and, if necessary, remove the final hydrogen sulphide by another method such as adsorption on metal oxides. Advantages are that the technology is very controllable and works reliably even when both the quantity of biogas and biogas quality fluctuate greatly, e.g. when using several different substrates. Chemical oxidative scrubbing is a proven method, but requires elaborate process control and knowledge of dealing with the chemical agents used. Compared with other desulphurisation methods, the specific costs of this technology are competitive. The process can be highly automated, with low labour input, and is regarded as reliable.

1.1.4 Adsorption on metal oxide or activated carbon

Hydrogen sulphide can be effectively removed from biogas by adsorption on the surface of metal oxides, such iron oxide, zinc oxide or copper oxide, but also on active carbon or ferric hydroxide (Ryckebosch et al., 2011; TU Wien, 2012a, 2012b). When hydrogen sulphide is adsorbed on metal oxides, the sulphur is bound as metal sulphide and water vapour is released. The adsorbent material must be replaced with fresh material when it becomes saturated. For systems where the adsorption of hydrogen sulphide occurs on activated carbon, a small addition of oxygen is usually made in order to oxidise the adsorbed gas to sulphur and bind it more strongly to the surface. If addition of oxygen is not possible, a specially impregnated activated carbon material can be used. For the impregnation, e.g. potassium iodide or sulphuric acid can be used (Persson et al., 2006; Ryckebosch et al., 2011). An advantage with this desulphurisation technique is that the concentration of hydrogen sulphide can be lower than 1 ppm. However, the overall specific costs of this technology are significantly higher than for other desulphurisation techniques, in spite of the relatively low investment costs. Overall, this makes this technique primarily suitable for use in final desulphurisation or when the input sulphur content of the raw biogas is low (typically up to 150 ppm).

1.1.5 Removal of hydrogen sulphide along with carbon dioxide

The separation of carbon dioxide from the raw biogas with water scrubbing also reduces the concentration of hydrogen sulphide (Ryckebosch et al., 2011; TU Wien, 2012a, 2012b). The same applies if the scrubbing fluid is a chemical substance, e.g. monoethanolamine, diethanolamine or methyldiethanolamine. The disadvantage of scrubbing with a chemical substance for sulphur removal is that a higher temperature is required for regeneration than if only carbon dioxide is removed, so energy consumption is higher. The advice is therefore that the hydrogen sulphide should be removed before the amine scrubber. Membranes can be used for removal of hydrogen sulphide along with carbon dioxide, but that would require a subsequent step for final hydrogen sulphide removal, e.g. with iron oxide. Pressure swing adsorption (PSA) cannot be used for hydrogen sulphide removal, since even small amounts of hydrogen sulphide in the gas can damage the adsorbent irreversibly (unrecoverable).

Table 2 shows the expected content of hydrogen sulphur in the effluent gas and the degree of separation for different techniques.

Table 2. Characteristics of different technologies for separation of hydrogen sulphide from biogas (Persson et al., 2006; Ryckebosch et al., 2011; TU Wien, 2012a, 2012b)

Type of technology for sulphur removal	H_2S content in the effluent gas, ppm	Degree of separation, %
Biological desulphurisation – oxidation in the anaerobic digester	100-300^{b}, 50^{c}	80-99^{b}, 95^{c}
Biological desulphurisation – oxidation in biological scrubbers	100-300^{b}, 50-100^{c}	
Process internal desulphurisation with metal salts ($FeCl_3$, $FeCl_2$, $FeSO_4$)	100-150^{c}	
Chemical oxidative scrubbing, sodium hydroxide	5^{a,d} ca 50^{a,e}	
Adsorption on metal oxides	-	> 99^{b}
Adsorption on activated carbon	< 1^{a}-3^{b}	

[a]Source: TU Wien (2012a, 2012b); [b]Source: Ryckebosch et al. (2011); [c]Source: Persson et al. (2006); [d]Possible to reach during stable operation; [e]Optimal economic operation.

1.2 UPGRADING TO SYNGAS

There are several methods for reforming methane to syngas; partial oxidation where methane and oxygen react, steam reforming where methane and water react, carbon dioxide reforming where methane and carbon dioxide react, auto thermal reforming where methane, oxygen and water or carbon dioxide react, and combined steam and carbon dioxide reforming where methane, carbon dioxide and water react. For some technologies, it is necessary to remove the carbon dioxide first. Reforming methods have different advantages and disadvantages depending on the reactants involved, the operating conditions and the resulting H_2:CO ratio in the syngas. They fit differently into the biogas system and have differing propensity for coke formation on the catalyst and different thermal properties. All this together has a major impact on the choice of appropriate reforming method in a given situation and whether it is possible to use raw or upgraded biogas.

1.2.1 Removal of carbon dioxide

In several of the existing technologies, it is best if carbon dioxide is removed prior to reforming, as it does not take place in the reaction and only dilutes the gas, requiring larger volumes to be treated. There are several commercial technologies for carbon dioxide removal available and they are often integrated with sulphur removal, commonly applied e.g. within the chemical industry and in upgrading of raw biogas and natural gas to vehicle or grid quality. In principle, the carbon dioxide removal technologies can be divided into (Andriani et al., 2013):

- Water scrubbing
- Chemical scrubbing/chemical absorption
- Physical scrubbing/physical absorption
- Pressure swing adsorption (PSA)
- Membrane-based techniques
- Biological techniques (using bacteria or microalgae)
- Cryogenic separation

There is a great deal of literature available on the different technologies for carbon dioxide removal and their advantages and disadvantages, including purity of the resulting gas, costs and energy use for the process, see e.g. Andriani et al. (2013), Bauer et al. (2013) and TU Wien (2012a, 2012b).

Water scrubbing is one of the most commonly used technologies, as it is relatively simple in design and is reliable. However, other technologies show good characteristics, e.g. amine scrubbers give high purity gas and very low methane slip. Regarding PSA and membrane units, the investment costs for these are about the same as for scrubbers and recent developments concerning the membrane units make it possible to achieve low methane slip (Bauer et al., 2013).

1.2.2 Partial oxidation

In partial oxidation (incomplete combustion), methane and oxygen react under sub-stoichiometric conditions, i.e. there is not enough oxygen for complete combustion. This is an exothermic reaction, releasing energy in the form of heat. Carbon monoxide and hydrogen gas are formed by reaction (1).

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2\,H_2 \qquad \Delta H^\circ_{298} = -36 \text{ kJ mol}^{-1} \qquad (1)$$

For comparison, it should be noted that complete oxidation of methane, i.e. complete combustion, is significantly more exothermic (reaction 2).

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad \Delta H^\circ_{298} = -890\ \text{kJ mol}^{-1} \qquad (2)$$

Partial oxidation can be carried out either with or without a catalyst. The feedstock for these types of reactors can be almost any carbonaceous material, from natural gas through liquid feeds such as fuel oils and gas oils to coal (Rice & Mann, 2007). Partial oxidation of solid biomass (i.e. gasification) is treated further in section 3.1.

Thermal partial oxidation of methane is run at a temperature of 1200-1600°C, with a flame temperature exceeding 2000°C (Aasberg-Petersen et al., 2001; Hägglund, 2006). The reaction takes place in a specially designed burner in which pure oxygen or enriched air is supplied. It is important that the temperature is kept high to ensure that all the methane is converted and to avoid soot formation as much as possible. If soot is formed, the synthesis gas must be purified in a scrubber at a later stage. In practice, a H_2:CO ratio of 1.7-1.8 is often obtained, which is lower than the theoretical value of 2.0. It is not possible to add water vapour in thermal partial oxidation, as this leads to increased soot formation. However, the H_2:CO ratio can, if necessary, be increased in a subsequent separate water gas reactor where steam is added (see reaction 4 in section 2.2.3).

Partial oxidation can be done in a reactor containing a catalyst, often based on nickel (Ni) or rhodium (Rh) (Joensen & Rostrup-Nielsen, 2002; Hägglund, 2006). When a catalyst is used, no burner is needed. The reaction takes place mainly according to reaction (1) above. However, the process is very complicated and side reactions occur whereby carbon monoxide and hydrogen gas are further oxidised to carbon dioxide and water (for most catalysts). This in turn leads to further reactions in the form of steam reforming, the water gas reaction and carbon dioxide reforming (reactions 3, 4 and 5, respectively) (Lunsford, 2000; Hägglund, 2006). The syngas leaving the reactor is nearly in thermodynamic equilibrium (Aasberg-Petersen et al., 2001; Hägglund, 2006). Partial oxidation is not suitable for raw biogas that also contains carbon dioxide. One advantage of the catalytic partial oxidation process is the exothermicity of the reaction, which means there is no need for an external heat supply, significantly reducing the costs (Izquierdo et al., 2012). Another advantage is that partial oxidation reforming produces syngas at a H_2:CO ratio of 1:1, which is highly suitable for liquid fuel synthesis (Anderson & Lin, 2013).

The major disadvantage with partial oxidation (both thermal and catalytic) is the reactivity of hydrogen and carbon monoxide with oxygen. Both products can be further oxidised to produce carbon dioxide and water (Anderson & Lin, 2013). Therefore, this particular method is only suitable for reactors with extremely short residence times. Another major drawback with partial oxidation is that it requires a feed stream of pure oxygen into the system, which is highly expensive, up to 40% of the cost of whole syngas production plant. Technologies such as inexpensive oxygen production processes (e.g. membranes) or the use of air as the oxidant are costly to install and not yet well-developed, and therefore partial oxidation is only used when cheap local oxygen is available (Eliseev, 2009).

Rice and Mann (2007) estimated that by that year, about fifty commercial thermal partial oxidation units had been built and operated on various feedstocks worldwide.

1.2.3 Steam reforming

In steam reforming, methane and steam react in an endothermic reaction (i.e. heat needs to be supplied) above a suitable catalyst to form syngas. This reaction (3) is basically reversible, but by allowing it to take place at a high temperature (850-900°C), low pressure (about 10 bar) and a relatively high steam:carbon ratio, nearly complete methane conversion can be obtained (Joensen & Rostrup-Nielsen, 2002; Hägglund, 2006).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H°_{298} = 206 \text{ kJ mol}^{-1} \qquad (3)$$

Besides reaction (3), the so-called water gas reaction (4) takes place during steam reforming. Since this is a reversible reaction, the resulting syngas contains water vapour, carbon dioxide and a fraction of the remaining methane, in addition to the desired carbon monoxide and hydrogen (Joensen & Rostrup-Nielsen, 2002; Hägglund, 2006). The resulting gas mixture composition is very close to the theoretical at the equilibrium for the applicable pressure and temperature.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H°_{298}= -41 \text{ kJ mol}^{-1} \qquad (4)$$

In steam reforming there is an increased risk of undesirable coke formation on the catalyst, which leads to a reduced catalytic effect. The rate of coke formation is determined by the thermodynamic equilibrium and it is possible to define a critical steam:carbon ratio at a certain pressure and a certain temperature at which coke formation occurs. This critical point increases with increasing temperature. Several metals, such as iron, cobalt and nickel, can be used to catalyse the steam reforming of methane, but in practice nickel is used since it is the most cost-effective option (Joensen & Rostrup-Nielsen, 2002; Hägglund, 2006). Common operating conditions are temperatures of 800-900°C and pressures of 10-40 bar (Hägglund, 2006). In large-scale hydrogen production plants, the steam reformer is operated at high temperatures (900-1000°C) due to the strong endothermic character of the reforming reaction, while the shift reactor(s) run at low temperatures (150-400°C) to maximise the hydrogen output (Kolbitsch et al., 2008).

Steam reforming of methane is the process that is almost exclusively used to produce syngas commercially at the present time (Abashar, 2004; Anderson & Lin, 2013). However, steam reforming of methane has its drawbacks, as it is a very endothermic (ΔH^0_{298}=206 kJ mol^{-1}) reaction and so it must be carried out at high temperature, thus requiring substantial energy and capital investment to sustain a high throughput process (Kolbitsch et al., 2008; Anderson & Lin, 2013). The catalyst and the reactor suffer from the high operating temperature, which shortens their life (Abashar, 2004). Furthermore, the H_2:CO ratio produced in the reaction is 3:1, whereas synthesis of many fuels, especially those via the Fischer-Tropsch process, is more efficient if the H_2:CO ratio is as close to 1 as possible (Anderson & Lin, 2013).

1.2.4 Carbon dioxide reforming (dry reforming)

During carbon dioxide reforming, methane is allowed to react with carbon dioxide at high temperature and high pressure in an endothermic reaction over a nickel catalyst (Hägglund, 2006). This results in carbon monoxide and hydrogen being produced by reaction (5). This would be a promising alternative for raw biogas, with a composition of approximately 60% methane and 40% carbon dioxide.

The method has several similarities to steam reforming, such as using a nickel-based catalyst and being a very endothermic process (see Table 3). This means that the same type of reactors as in steam reforming can be used, in similar operating conditions. Carbon dioxide reforming of methane results in a synthesis gas with a H_2:CO ratio of around 1.0 (see reaction 5), which in most cases is too low for direct use in e.g. a Fischer-Tropsch reactor. The H_2:CO ratio can be adjusted up to the desired level, for example in a separate water gas reactor (according to reaction 4), see section 2.2.3.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H°_{298} = 247 \text{ kJ mol}^{-1} \qquad (5)$$

The interest in this method has grown in recent years, as it utilises the carbon dioxide. This type of reforming is not yet at commercial scale, however, because of problems with coke formation on the catalyst, with reduced activity as a result. A promising alternative is to combine carbon dioxide reforming with steam reforming, in the so-called combined reforming process, which can reduce the above-mentioned problems with coke formation (Effendi et al., 2002; Hägglund, 2006). There are also nickel-based catalyst combinations that resist coke formation relatively well. Alternatively, the catalyst can be based on other metals that have superior resistance to coking than nickel, although these are significantly more expensive.

A major drawback of the dry reforming reaction is that it is highly endothermic, which makes the process energy-intensive and costly in terms of investment and operation (Mota et al., 2011). The rather high reaction temperature also causes sintering and deactivation of the catalyst. Another problem is the formation of carbonaceous deposits on the catalyst surface. According to Izquierdo et al. (2012), new catalytic systems are needed in order to avoid carbon deposition and to achieve higher conversion rates in the dry reforming process.

1.2.5 Autothermal reforming

Autothermal reforming can be done in two different ways, either by a combination of thermal partial oxidation and steam reforming (Hägglund, 2006; Amin & Yaw, 2007), or by a combination of thermal partial oxidation and carbon dioxide reforming (Izquierdo et al., 2012). Common to both types of autothermal reforming is that the process can be completely energy balanced (hence the name autothermal) by adjusting the amount of incoming oxygen and water vapour or carbon dioxide. In the first approach, reactions 1, 3 and 4 are combined, while in the second approach reactions 1 and 5 are combined. Furthermore, in the same way as for catalytic partial oxidation, a number of other reactions take place in complex reforming. For both approaches, reactor design can be made relatively simple, with lower investment costs as a result, because heat does not need to be transported to or from the reactor.

In the first approach (with steam), easy control of the H_2:CO ratio, soot-free synthesis gas, high flow rates and lower temperatures than in the partial oxidation process are some of the benefits (Hägglund, 2006; Amin & Yaw, 2007). In this approach, technically a gas mixture consisting of methane, water vapour and oxygen (air or pure oxygen) is flamed at sub-stoichiometric conditions in a burner. The resulting gases then flow down through a reactor, where they pass through a catalyst bed in which further reactions help the gases to reach equilibrium. The catalyst bed may be based on nickel. The catalyst bed also prevents soot formation that would otherwise be unavoidable when using only partial oxidation (Ernst et al., 2000; Hägglund, 2006; Amin & Yaw, 2007). The thermodynamic equilibrium when the gas leaves the reactor determines its composition at the outlet

(Aasberg-Petersen et al., 2001; Hägglund, 2006; Amin & Yaw, 2007). The temperature in the reactor catalyst bed is typically 900-1100°C (about 1900°C in the combustion chamber) and the operating pressure is typically 12-70 bars. There are also fluid bed reactors. The autothermal reforming technology has been commercially available since the late 1950s. Most of what is mentioned above is probably also valid for the second autothermal reforming approach (with carbon dioxide), but there is a lack of literature.

In autothermal reforming (the first approach, with steam), the H_2:CO ratio of the syngas produced may in theory be varied approximately between 2 and 3.5 (Hägglund, 2006). The H_2:CO ratio depends on the pressure and temperature at the outlet of the reactor and the relationship between incoming amounts of methane, water vapour and oxygen. As for steam reforming, the steam:carbon ratio is a critical factor. A low steam:carbon ratio is often desirable, as this lowers the H_2:CO ratio to the level desirable in subsequent processes, e.g. in the Fischer-Tropsch process a H_2:CO ratio of 2.1 is desirable. However, too low a ratio raises the risk of coke formation. The H_2:CO ratio can also be lowered by addition of a suitable amount of carbon dioxide to the input process gases. This type of autothermal reforming is not suitable for raw biogas that also contains carbon dioxide.

In the second approach for autothermal reforming (with carbon dioxide), it is possible to achieve a thermoneutral process by controlling the methane:carbon dioxide:oxygen ratio, when partial oxidation (which is an exothermic reaction) is combined with carbon dioxide reforming (which is an endothermic reaction) (Izquierdo et al., 2012). Moreover, the presence of oxygen at high temperatures makes it possible to avoid carbon deposition in the catalyst.

Although autothermal reforming is an old idea, there are only a few commercial sites. Experience in commercial plants has shown that the formation of soot can adversely affect the overall unit operation (Rice & Mann, 2007).

1.2.6 Combined steam and carbon dioxide reforming

Adding water vapour in carbon dioxide reforming reduces the share of carbon in the process gas, which in turn reduces the risk of coke formation (Effendi et al., 2002; Hägglund, 2006). This process can be carried out in the same type of reactors as for carbon dioxide reforming and steam reforming and remains highly endothermic (see Table 3), with the active reactions 5, 3 and 4. Besides reduced carbon formation, the process also has the advantage that the H_2:CO ratio of the syngas produced can be controlled relatively easily by adjusting the amounts of water vapour and carbon dioxide added. In this way, the H_2:CO ratio can in theory be varied between 1.0 and about 3.5. Combined steam and carbon dioxide reforming is suitable for raw biogas that also contains carbon dioxide.

As mentioned, combined carbon dioxide and steam reforming avoids carbon deposition on the catalyst, which is otherwise a major problem in dry reforming (Kolbitsch et al., 2008). Furthermore, if the reforming is performed at high temperatures, unreacted oxygen in the synthesis gas is also avoided. Therefore, the resulting syngas consists of unreacted methane, carbon dioxide, carbon monoxide and hydrogen and excess water. When high ratios of water to methane and high reactor temperatures are applied, the equilibrium concentration of methane is negligible. The excess water can be removed by condensation. However, the energy demand increases very rapidly because of the high energy demand to evaporate and superheat the excess water.

1.2.7 Plasma reforming

In plasma reforming, the same type of methane reforming reactions as discussed in the preceding sections are employed, but with the difference that the energy for initiating these reactions is supplied by energy added to an electric arc, rather than by external heat (a flame) or the influence of a catalyst (Czernichowski, 2001: Hägglund, 2006). In plasma reforming, no catalyst is needed and the reactions in the reactor can be run at a temperature below 1200°C and a pressure below 6 bar (Nam Chun et al., 2004; Hägglund, 2006). The technology is not yet commercially available.

1.2.8 Some operating modes, simulation calculations

Table 3 summarises all the reactions for the different reforming methods described and the resulting H_2:CO ratio for each method under common operating conditions. In all cases it is assumed that the incoming gas is preheated to 400°C. Data on the gas composition of the synthesis gas output were taken from a study which used equilibrium calculations in FactSage (Hägglund, 2006). Table 3 also shows the reaction enthalpy under the assumed operating conditions for the respective reforming method specified, with only the autothermal reforming being exothermic in the given conditions. The high exhaust temperature in partial oxidation makes the reaction somewhat endothermic at the theoretical oxygen:methane ratio of 0.5. This reaction is slightly less endothermic if the input gases are preheated to a higher temperature. To completely avoid the need for addition of external heat to the process, it is possible to raise the oxygen:methane ratio to e.g. 0.65 (see Table 3), which gives a synthesis gas H_2:CO ratio of about 1.8. The yield will then be somewhat lower due to the formation of more water and carbon dioxide.

Table 3. Operating conditions, overall reaction and H_2:CO ratio of the synthesis gas produced for the five most common methane reforming methods (calculated in FactSage by Hägglund, 2006)

Reforming method	H_2:CO ratio
Partial oxidation (PO):	
(400→1400°C, 50 bar, $\Delta H_r = 61.7$ kJ/mol)	≈ 2.0
$CH_4 + 0.5\ O_2 \rightarrow 1.89\ H_2 + 0.96\ CO + 0.04\ CH_4 + 0.03\ H_2O$	
(400→1400°C, 50 bar, $\Delta H_r = -1.7$ kJ/mol)	≈ 1.8
$CH_4 + 0.65\ O_2 \rightarrow 1.73\ H_2 + 0.95\ CO + 0.26\ H_2O + 0.04\ CO_2$	
Steam reforming (SMR):	
(400→850°C, 10 bar, $\Delta H_r = 196$ kJ/mol)	≈ 3.5
$CH_4 + H_2O \rightarrow 2.06\ H_2 + 0.59\ CO + 0.34\ CH_4 + 0.27\ H_2O + 0.07\ CO_2$	
Carbon dioxide reforming (COR):	
(400→850°C, 10 bar, $\Delta H_r = 213$ kJ/mol)	≈ 1.2
$CH_4 + CO_2 \rightarrow 1.35\ H_2 + 1.17\ CO + 0.32\ H_2O + 0.26\ CO_2 + 0.16\ CH_4$	
Autothermal reforming (ATR):	
(400→1050°C, 20 bar, $\Delta H_r = -4.2$ kJ/mol)	≈ 2.3
$CH_4 + 0.6\ O_2 + 0.6\ H_2O \rightarrow 1.92\ H_2 + 0.83\ CO + 0.66\ H_2O + 0.16\ CO_2 + 0.01\ CH_4$	
Combined steam and carbon dioxide reforming (SMR+COR):	
(400→850°C, 15 bar, $\Delta H_r = 304$ kJ/mol)	≈ 1.5
$CH_4 + 1.6\ H_2O + 1.3\ CO_2 \rightarrow 2.07\ H_2 + 1.39\ CO + 1.26\ H_2O + 0.78\ CO_2 + 0.13\ CH_4$	

1.2.9 Catalysts

Catalysts play a key role in biogas-to-syngas production. Catalysts increase efficiency, but can also give technical problems and represent a major financial cost. Nickel catalysts are highly active for reforming reactions and cost much less than noble metal catalysts, which makes them suitable for a cost-effective commercial reforming process (Mota et al., 2011). Unfortunately, nickel is more prone to carbon deposition, sulphur poisoning and sintering. It is also important to remove hydrogen sulphide prior to the reforming process since it poisons nickel catalysts, leading to very low reforming activity (Effendi et al., 2005).

Design and composition of a catalyst have a large impact on its reforming activity and resistance to coking and sintering (Tsyganok et al., 2003; Guo et al., 2004). The incorporation of a second metal into carbon dioxide reforming catalysts is a common practice designed to improve stability. Adding small amounts of noble metals such as ruthenium, platinum, palladium, iridium and rhodium to nickel-based catalysts has been studied (Mota et al., 2011). The characteristic of a catalyst has a large influence on its performance. Amending nickel/magnesium oxide (MgO) with potassium greatly improves the stability of these catalysts in carbon dioxide reforming of methane (Frusteri et al., 2001). Indeed, potassium addition alters both the electronic and geometric properties of the nickel/magnesium oxide system, most likely inducing high resistance against coking and sintering, respectively. Adding cerium oxide (CeO_2) as an additive promoter on nickel/aluminium oxide (Al_2O_3) catalysts for carbon dioxide reforming provides significantly higher reforming reactivity and resistance to carbon deposition compared with conventional nickel/magnesium oxide (Laosiripojana & Assabumrungrat, 2005; Laosiripojana et al., 2005).

1.2.10 Comparative analysis of technologies for reforming of methane

An overview of the advantages and disadvantages of the different technologies is given in Table 4. Of the technologies reviewed, steam reforming and partial oxidation (with or without catalytic converter) are currently the most commonly used methods in commercial applications to produce syngas using natural gas as feedstock (Hägglund, 2006).

Autothermal reforming (with carbon dioxide or steam) and combined steam and carbon dioxide reforming are the technologies that have most benefits, such as reduced coke formation on the catalysts. In these reforming approaches where two processes are combined, the H_2:CO ratio can also be governed more easily and within a wider range than in the reforming methods where only one process is involved. In autothermal reforming, the process can also be fully balanced in terms of energy by adjusting the amount of incoming oxygen and water vapour (or carbon dioxide), which can simplify the reactor design, as heat does not need to be added or taken away from the reactor. Combining two different reforming methods also seems to work well in practice.

For these technologies (autothermal with carbon dioxide and combined steam and carbon dioxide reforming), carbon dioxide is included in the constituent gases, which is an advantage when biogas that is composed of methane and carbon dioxide is used as the raw material. The carbon dioxide is used as a carbon source in the reforming. This means that the biogas does not need to be upgraded to the extent that the carbon dioxide is removed, which is an advantage both in terms of costs (one process step less) and product yield.

However, reforming processes including oxygen are capital- and cost-intensive because they also need a process to produce pure oxygen, most commonly from air. The reason for using pure oxygen and not air for partial oxidation and autothermal reforming is to avoid dilution of atmospheric nitrogen in the resulting syngas, which lowers the heating value (Wilhelm et al., 2001). Furthermore, the nitrogen gas (i.e. the air) has to be compressed before it enters the reactor in which reforming takes place, for which much compression energy is needed. Moreover, the thermal efficiency is lower when atmospheric nitrogen is included.

Overall, this suggests that autothermal reforming and combined steam and carbon dioxide reforming are promising technologies when biogas feedstock is used as raw material for syngas production, if cheap oxygen is available. In time, plasma reforming can become interesting because of lower costs, but this technique probably needs to evolve more before it is ready for commercial use.

Table 4. Comparison of syngas production technologies (after: Lunsford, 2000; Wilhelm et al., 2001; Zhang et al., 2004; Effendi et al., 2005; Hägglund, 2006; Amin & Yaw, 2007; Kolbitsch et al., 2008; Mota et al., 2011; Izquierdo et al., 2012; Anderson & Lin, 2013). PO = partial oxidation; SMR = steam reforming; COR = carbon dioxide reforming (dry reforming); ATR autothermal reforming

	Advantages	Disadvantages
PO (thermal)	- Desulphurisation of feedstock not required - No catalyst, therefore lower syngas CO_2 content - Low methane slip	- Reactivity of hydrogen and carbon monoxide with oxygen - Need for pure oxygen => higher costs - Low H_2:CO ratio - High process temperature - Low syngas methane content
PO (catalytic)	- Exothermicity, no need for external heat supply - No heat supply => lower investment and costs - Low methane slip	- Soot is formed during the process - High risk of carbon deposits building up - High risk of catalyst deactivation - Reactivity of hydrogen and carbon monoxide with oxygen - Need for pure oxygen => higher costs - Low H_2:CO ratio - High process temperature - Low syngas methane content - Not suitable with unprocessed biogas
SMR	- Steam results in strong inhibition of carbon deposit formation - Almost complete methane conversion - No need for oxygen, - Process almost exclusively used to produce syngas commercially - Extensive industrial research - Lowest process temperature of all reforming methods - Best H_2:CO ratio for hydrogen production applications - Works under some process conditions with unprocessed biogas, e.g. combined carbon dioxide and steam reforming	- Strong endothermic character - Operation at high temperatures - Wear of catalyst and reactor - High energy need - High capital costs - High H_2:CO ratio = 3:1 - Sensitivity to sulphur - Highest atmospheric emissions of all reforming methods - Not all process conditions work with unprocessed biogas
COR	- Works with unprocessed biogas - Small noble metal addition, such as Rh, Pt or Pd, can improve the catalyst stability and reducibility - Addition of rare-earth oxides such as CeO_2 and ZrO_2 give better properties of nickel catalysts	- Strong endothermic character - High energy need - High capital costs - Catalysts prone to carbon deposition - Catalysts prone to sintering - Accompanied by several potential side reactions - e.g. water formation as a side product indirectly reduces the syngas selectivity and lowers the H_2:CO ratio
ATR = PO + SMR	- Carbon deposition avoided - Thermoneutral process - Lower temperature than for partial oxidation - Relatively simple reactor design - Lower investment costs - Low methane slip	- Limited commercial experience - Usually requires oxygen? - Does not work with unprocessed biogas?
ATR = PO + COR	- Works with unprocessed biogas - Carbon deposition avoided - Thermoneutral process - Lower temperature than for partial oxidation - Relatively simple reactor design - Lower investment costs - Low methane slip	- Limited commercial experience - Usually requires oxygen
SMR+ COR	- Works with unprocessed biogas - Carbon deposition avoided - H_2:CO ratio can be controlled relatively easily by the amounts of water and carbon dioxide added	- Unreacted CH_4, CO_2 and H_2O in syngas - Hydrogen-rich synthesis gas - High energy need - High capital costs - High energy demand to evaporate and superheat the excess water

THERMOCHEMICAL ROUTES TO SYNGAS

In this chapter we provide a brief introduction to agricultural biomass conversion to syngas via the thermochemical routes of pyrolysis and gasification. The technologies are very briefly described and their suitability for some agricultural feedstocks is discussed. The intention of this descriptive chapter is to enable a comparison in the discussion section with the anaerobic digestion-to-syngas route.

1.3 THERMOCHEMICAL GASIFICATION

Thermochemical gasification is a process for converting carbonaceous feedstock into gaseous products. The gasification technology involves high temperatures, generally in the range 600-900°C or even higher in a reducing (oxygen-deficit) atmosphere (Richardson et al., 2012). Partial oxidation of the biomass takes place in the presence of a gasifying agent (e.g. air, oxygen, steam, carbon dioxide, or mixtures of these components), resulting in the production of a gas made up primarily of carbon monoxide and hydrogen (more than 85% by volume) (Hackett et al., 2004). The end use of the raw gas includes co-firing, firing, Stirling engines, gas engines, gas turbines, fuel cells, upgrading to hydrogen or syngas, and others (Abuadala & Dincer, 2012).

Syngas is obtained after suitable purification and conditioning stages of the raw gases (Figure 3). A considerable share of syngas production costs is assigned to the purification and conditioning of raw gases. The raw gas produced by gasification is mainly composed of carbon monoxide, hydrogen, methane, carbon dioxide, water and nitrogen (if air is used as the oxidising agent), but it also contains secondary products such as tars, inorganic compounds (alkali metals, nitrogen, sulphur and chlorine compounds) and solid particles. Among the contaminants of biomass gasification-derived raw gas, tars remain the most troublesome (Richardson et al., 2012).

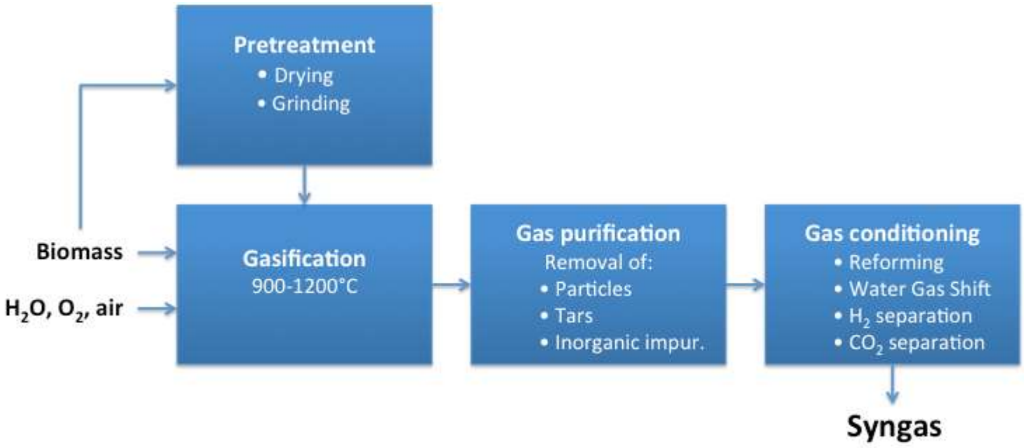

Figure 3. Schematic diagram of the multi-stage production process of syngas from biomass gasification. After Richardson et al. (2012).

The contact between the solid fuel particles and gases takes place in the gasifier. Gasifiers come in many different varieties, e.g. entrained flow, fixed bed and fluidised bed. Two types of fluidised bed gasifiers are common; bubbling fluidised bed gasifiers, where the bed material is fluidised or agitated by gases flowing through it, and circulating fluidised bed gasifiers, where the bed material circulates. Depending on the design specification, fuel can be fed into the top, bottom or middle of the gasifier.

Gasification is an endothermic process and therefore heat needs to be supplied to the gasification process (Abuadala & Dincer, 2012). Heat can be generated directly by adding a small amount of air or oxygen to the gasifier to combust some of the biomass. Air-blown gasification is the least expensive option, and this process is well-suited for power production. However, large amounts of nitrogen are present in the syngas produced, which makes this process less suitable if the syngas is intended for catalytic synthesis of transportation fuels. Oxygen-blown systems avoid nitrogen dilution, but have the disadvantage of requiring an expensive oxygen production step (see more in section 2.2.2, Partial oxidation). Furthermore, the additional carbon dioxide formed in a direct process will most likely require further removal prior to fuel synthesis (Carpenter et al., 2010). For indirectly heated gasifier systems, the heat is provided by combusting some of the feedstock, char or clean syngas in a separate reactor and transferring heat through exchangers. The choice of gasifier or reactor type for gasification depends on the capacity of the unit, and its specification has to suit the end use or its downstream utilisation system (Abuadala & Dincer, 2012).

So far, biomass gasification for syngas projects remains at the pilot or demonstration scale (Heyne et al., 2013). Technical barriers to large-scale biomass gasification are dependent on type of technology used, but include e.g. fuel pre-treatment and fuel feeding, tar-related problems, aspects of pressurisation, particle and gas separation, gas upgrading and oxygen supply (Heyne et al., 2013). Most research and development in gasification technology has focused on wood or wood residues. There are however several other agricultural products, wastes and residues that can be utilised, such as short rotation forestry, different energy crops, straw, nuts and nutshells, corn cobs and stovers, etc. In Sweden, straw from cereal production and short-rotation coppiced willow (Salix) biomass have been identified as promising alternatives in terms of cost, availability and access to suitable machinery and logistical systems (Ahlgren, 2009).

In general, feedstock for gasification has to meet several technical specifications. Depending on gasification technology, different properties of the feedstock are more or less important. For indirect gasification, more volatile substances and less coke is desirable and therefore **ash content** is important. Ash is also important for fluidised bed gasification, as low **ash melting point** can be a problem. The content of e.g. active silicon, phosphorus and calcium also affects the ash melting behaviour. **Moisture content** should be below 10-20% for syngas production. Entrained flow gasifiers require a lower moisture content than fluidised bed gasifiers. Drying is often needed and could preferably be integrated into the gasification process. **Metals** are detrimental as they cause corrosion and sintering of bed material in fluidised bed gasifiers. Desired **particle size** depends on the gasification process, but in general the size must not vary much. Entrained flow gasification is particularly sensitive to particle size variations and requires a powder-like feed (particle size typically lower than 0.5 mm) but large fractions of too fine material may also cause problems. Fluidised bed gasifiers are more tolerant to feed quality changes and larger particle sizes, up to 50 mm for bubbling fluidised bed gasifiers (Joelsson, 2013).

Gasification of agricultural residues such as straw is regarded as more complicated than e.g. gasification of wood fuel due to its high content of potassium and chlorine, components that can give rise to deposits and corrosion. Straw also has a high ash content, which can give problems with sintering and deactivation of the catalyst (Skøtt & Hansen, 2000). Furthermore, the structure of the straw fuel complicates handling and the feed system to the gasifiers. However, a number of studies and demonstration projects have confirmed that straw is a promising fuel for gasification. In

Denmark, successful tests with straw gasification have been carried out since the 1980s (Hansen, 2012). Much research on straw is also being carried out in China, e.g. the use of rice straw (Zhang et al., 2013).

Salix has a relatively high content of potassium and chlorine, which can lead to problems with sintering, supplements and corrosion. Combustion plants can be fuelled by up to 100% Salix without major problems, although in practice mixtures of 10-15% willow are more normal. Salix can also have higher concentrations of heavy metals, especially cadmium, than most other biomass types. This is good from a soil decontamination perspective, as Salix takes up cadmium from the soil and it is removed with the harvested biomass. The cadmium content in Salix can be up to ten times higher per kg dry matter than that in e.g. forest fuels and straw. Salix is a woody fuel and is usually handled as chips, which facilitates mixing with other types of wood fuels (Nilsson & Bernesson, 2008).

1.4 PYROLYSIS

Pyrolysis is thermal decomposition occurring in the absence of oxygen. In the pyrolysis process, the biomass feedstock is heated to between 400 and 800°C under anaerobic conditions, resulting in decomposition that produces bio-oil (condensable), gas (non-condensable under ambient conditions) and charcoal (solid char). Pyrolysis is currently used in several commercial plants and the purpose of these plants is often to produce one specific product, either bio-oil or charcoal. The yield ratio of the pyrolysis products depends on several process variables, e.g. pre-treatment, heating rate, temperature and residence time. Typically, a lower heating rate (slow pyrolysis) favours the formation of charcoal, while a high heating rate (fast and flash pyrolysis) increases the formation of bio-oil (Bojler Görling et al., 2013).

Gases from pyrolysis include methane, hydrogen, carbon monoxide and carbon dioxide. The gases can be upgraded to syngas quality, but most past research on pyrolysis has focused on the production of liquid fuel (bio-oil) as the main product, while the study of gas applications and of biochar has received much less attention. However, upgrading of pyrolysis gases has many similarities to upgrading of gasification gases (Adrados et al., 2013). The bio-oil and charcoal from the pyrolysis process can also be gasified to produce syngas.

In general, feedstock for pyrolysis has to meet several technical specifications. Impurities are detrimental to the pyrolysis process, so rocks and metal parts must be removed. The effect of impurities in large-scale applications has not yet been totally clarified, however. High levels of extractive substances in the raw material can reduce the yield. Pyrolysis processes require the moisture content to be below 10%. Variations in moisture are generally also a problem. In fast pyrolysis, particle size should be small (<3 mm). In general, a homogeneous feedstock is desirable, since variations in feedstock properties can cause undesired variations in the properties of the end products (Joelsson, 2013).

Agricultural crops cultivated on fallow land and by-products are considered to be potential feedstocks that would not cause significant competition with food production. However, biomass originating from agricultural land usually has a low ash melting point and a high content of alkali metals and ash. This will cause operational problems (e.g. poisoning of catalysts) in conventional gasification at high temperature. Low-temperature pyrolysis of biomass is therefore an interesting alternative to gasification, since alkali metals would remain in the charcoal (biochar) and the formation of persistent tar compounds would be minimised. This would permit the use of feedstock with a high alkali and ash content, such as agricultural crops and by-products, for fuel production. Pyrolysis of biomass at relatively small scales and remote locations enhances the energy density of the biomass resource and reduces energy requirements and costs related to handling and transport (Bojler Görling et al., 2013).

In a report by Bojler Görling et al. (2013), different agricultural feedstocks were studied as raw material for pyrolysis. The authors found that short rotation Salix was one of the most promising alternatives. Its chemical properties regarding alkali and ash content are unlikely to cause any problems for low-temperature pyrolysis, and the production costs are competitive in comparison with those of many other feedstocks. There is also long experience of cultivation of Salix and well-developed agricultural machinery.

ENERGY ANALYSIS

The scope of this report did not allow for a full energy analysis and therefore the analysis reported here provide very rough estimates, which should only be seen as indicative. The energy analysis includes the energy used in various reforming processes and their need for biogas of different quality (upgraded or not upgraded) and energy need for pure oxygen. The net energy was calculated as outgoing energy – ingoing energy per kg methane. The energy balance was calculated as the energy (lower heating value) of the outgoing gases (hydrogen, carbon monoxide and methane) divided by total energy input. The energy balance was also calculated when the methane in the process was included in the calculations.

The energy analysis (Table 5) was to a large extent based on the reactions and associated enthalpy values (ΔH_r) listed in Table 3. The calculations were based on 1 kg methane and the yield of syngas was calculated using stoichiometric methods. The reforming energy was calculated based on the reactions and enthalpies listed in Table 3, assuming an efficiency of 90%. Input energy for biogas upgrading, desulphurisation and oxygen production (Table 5) were calculated from values given by Börjesson and Berglund (2006), Lantz (2013) and Sapali and Raibhole (2013). Regarding the energy consumption for production of oxygen, a purity of 96.2% on a molar basis extracted from air by cryogenic methods (0.257 kWh Nm^{-3} O_2) was assumed (data from Sapali & Raibhole, 2013).

In the calculations (Table 5) many factors were omitted, e.g. heat losses during reforming, upgrading and desulphurisation of the biogas produced. Furthermore, no account was taken of the fact that some of the resulting gases might be returned to the process, lost or used for other ends than the intended purpose. In addition, no consideration was given to the amount of carbon dioxide in the reforming methods (COR and SMR+COR), for which the amount would need to be adjusted upward or downward to make the reforming function as intended (as optimal as possible). It should also be noted that when calculating energy balance, a number of assumptions needed to be made, which implies there are uncertainties in the results.

The output energy (as hydrogen, carbon monoxide and methane) from the reforming processes was largest from combined steam and carbon dioxide reforming and steam reforming (SMR+COR and SMR in Table 5). This was mainly due to high hydrogen yield (see Table 3). However, the energy input to these processes are larger than for the other technologies, due to very endothermic reactions in the reforming (see Table 3).

From Table 5 we can also conclude that energy for reforming dominate the process energy input, while energy use for upgrading biogas, desulphurisation and production of pure oxygen had marginal effects on net energy yield. This was especially evident for carbon dioxide reforming (COR), which had high reforming process energy needs and resulted in a low net energy yield and a relatively low energy balance. We can also conclude that when ingoing methane is included in the energy balance, the different reforming processes more or less have the same energy balance.

All together, combined steam and carbon dioxide reforming and steam reforming are interesting reforming methods to study in more depth for biogas applications. This is due to their high hydrogen production, high net energy yield and, in the case of combined steam and carbon dioxide, the fact that the reforming biogas does not have to be upgraded to be used as feedstock. Autothermal reforming is also an interesting technology that brings opportunities to use a simpler reforming reactor and thereby reduce process costs.

Table 5. Energy yield of various reforming methods for methane, taking into account the need for complete biogas upgrading or only sulphur purification of biogas and in some processes the production of pure oxygen needed for the process (reaction formulae are listed in Table 3)

Reforming process[a]	Energy in products out[b] (MJ/kgCH_4)	Energy O_2 production[c] (MJ/kg CH_4)	Process energy to reforming[d] (MJ/kgCH_4)	Energy for upgrading[e] (MJ/kgCH_4)	Energy for S removal[f] (MJ/kgCH_4)	Net energy[g] (MJ/kgCH_4)	Energy balance[h] (MJ_{out}/MJ_{in})	Energy balance incl. CH_4 in process[i] (MJ_{out}/MJ_{in})
PO I	48	0.65	4.3	3.9	Incl upgr[m]	39	5.4	0.81
PO II	43	0.84	Not relevant[k]	3.9	Incl upgr[m]	39	9.4	0.79
SMR	59	Not needed[j]	14	3.9	Incl upgr[m]	41	3.4	0.87
COR	49	Not needed[j]	15	Not needed[l]	0.77	34	3.2	0.75
ATR	44	0.78	Not relevant[k]	3.9	Incl upgr[m]	40	10	0.82
SMR+ COR	63	Not needed[j]	21	Not needed[l]	0.77	41	2.9	0.87

[a] Reforming process methods according to Table 3.

[b] Energy as lower heating value in H_2, CO and CH_4 gases leaving the reforming process, calculated as MJ per kg CH_4 entering the process (H_2, CO and some CH_4; 121.0 MJ kg^{-1}, 10.1 MJ kg^{-1} and 50.0 MJ kg^{-1}, respectively, at 15.4°C. Source: Wikipedia, 2013).

[c] Energy for cryogenic separation of oxygen from air calculated after Sapali and Raibhole (2013) as MJ per kg CH_4 entering the process. Calculated as energy consumption for production of oxygen with 96.2% purity on a molar basis from air by cryogenic methods (0.257 kWh Nm^{-3} O_2).

[d] Process energy for reforming assumed to be 90% of theoretical efficiency. The theoretical input process energy for reforming was calculated from the reaction enthalpy (ΔH_r) values in Table 3 for each reforming process, calculated as MJ per kg CH_4 entering the process. Endothermic reaction enthalpies result in positive values and exothermic reaction enthalpies in negative values. The 90% value was chosen because it is not unusual for a good furnace. Excess energy from the reforming assumed not to be utilised.

[e] Energy for upgrading of biogas (calculated after Börjesson and Berglund (2006) and Lantz (2013)). In this process, removal of sulphur is also included. Börjesson and Berglund (2006) state 0.11 MJ MJ^{-1} biogas (equivalent to 5.5 MJ kg^{-1} CH_4) and Lantz (2013) gives an approx. 30% lower value, so 3.85 MJ kg^{-1} CH_4 was used in the calculations.

[f] Energy for removal of sulphur from the biogas, assumed to be 20% of the energy for upgrading the biogas, calculated as MJ per kg CH_4 entering the process.

[g] Net energy (calculated as: Energy in products out - (Energy for upgrading or Energy for S removal + Energy O_2 production + Process energy to reforming)), calculated as MJ per kg CH_4 entering the process.

[h] Energy balance calculated as: Energy in products out / (Energy O_2 production (if needed) + Process energy to reforming + (Energy for upgrading or Energy for S removal)).

[i] Energy balance including methane entering the process calculated as: Energy in products out / (Energy in CH_4 entering the process (50.0 MJ kg^{-1}) + Energy O_2 production (if needed) + Process energy to reforming + (Energy for upgrading or Energy for S removal)).

[j] Oxygen not used in the reforming process and therefore not needed.

[k] Not relevant when more energy than used is produced in the reforming process (negative value in Theoretical input energy to reforming and in Table 3 for ΔH_r).

[l] Upgrading of biogas assumed not to be needed when the carbon dioxide produced in the biogas process can be used in the reforming process.

[m] Sulphur removal assumed to be included in the biogas upgrading process.

For gasification, product yields vary depending on the process configuration and type of feedstock. It is rather difficult to find data in literature on conversion efficiency to syngas; most studies report efficiency for gasification to hydrogen or other type of biofuels. However, Xie et al. (2012) study energy efficiency in syngas production, reporting maximum yield of syngas between 0.63 and 0.69 MJ syngas per MJ input feedstock (pine dust) for a two-staged integrated pyrolysis and gasification process. Börjeson et al. (2013) study production of synthetic natural gas via gasification of biomass, reporting a thermal efficiency between 39 and 70% for different gasifiers. In some cases electricity is co-produced, including the electricity significantly raises the efficiency of the process. According to a study by Spath and Dayton (2003) gasification can yield somewhere between 0.36 and 0.73 MJ hydrogen per MJ input biomass. A more recent review found that the reported hydrogen yield in process simulation varies between 38.9 and 76.3 kg H_2 per dry short ton biomass, rough recalculation of which gives a variation in yield of between 0.24 and 0.49 MJ hydrogen per MJ input biomass. This does not include any electricity or other energy products that might have been generated or consumed, which would have to be included in a calculation of net overall efficiency (NREL, 2011).

For comparison, we can study the yield of syngas via anaerobic digestion and reforming. According to Carlsson and Uldal (2009), every MJ input straw can yield approx. 0.65 MJ methane through anaerobic digestion (this was calculated for a long retention time in the digester and the figure may be lower in practice). Energy for the digestion process is not included. According to Table 5, about 0.8 MJ syngas can be obtained per MJ methane. This is with energy input included, since the reforming adds much energy. If energy input is not included, the yield of syngas will in some cases be higher than the energy input in methane, which will not be a fair comparison. However, this also makes comparison difficult; all the other yields discussed here are gross yield, i.e. without taking into consideration external energy inputs. In total this gives approx. 0.5-0.6 MJ syngas per MJ input straw, which is within the lower range of energy yields reported for gasification. Note that this is a very rough estimate, without consistent methodology. Furthermore, the yield of biogas is very different for different feedstocks, which can change the energy balance dramatically.

DISCUSSION AND CONCLUSIONS

As this report shows, there are many different technological pathways available for production of syngas from agricultural feedstock. It is impossible to say which is the preferred technical pathway. The final use of the syngas is of course a decisive factor. Furthermore, some technologies are commercially mature while others are still under development, so the preferred technical pathway in the future may be different than today. Availability and cost of feedstock, logistics, storage possibilities etc. can also be decisive. The scale of production and required investment can be another factor for choice of technology, as well as energy and environmental performance.

For the same reasons, comparison between anaerobic digestion with reforming and gasification is difficult. Feedstock can vary greatly, as can energy efficiency in conversion. Different feedstock are suitable for different technologies, e.g. wet and easily degradable material can be more suitable for the anaerobic route, while dryer and more lignin-containing material can be more suitable for thermochemical treatment. In conclusion, anaerobic digestion and gasification should not be seen as competing but as complementary technologies, providing opportunities for using a diversity of raw materials as feedstock for syngas production.

It could be of interest to compare the energy balance for the anaerobic digestion-to-syngas and the gasification-to-syngas technical pathways. This is not an easy task, however. In the previous chapter we reported a range of values for the conversion part alone and we did not include the entire life cycle of the technical pathways. It was also difficult to find a consistent methodology. However, our very rough estimates of the energy balance indicated that the anaerobic-to-syngas production route is within the lower range of energy yields reported for gasification. Energy for feedstock production and transportation was not included in this analysis. Using dedicated energy crops would give a very different energy balance than using wastes or residues. Furthermore, the systems yield different by-products, e.g. digestate from anaerobic digestion is a valuable farm nutrient source, which makes comparisons complex.

Syngas production from natural gas is a commercial-scale technology. Similar technology could be used for biogas applications. However, natural gas-based plants are very large-scale, so if these technologies are to be applicable for biogas they need to be down-sized. It was not possible to determine the technology most suitable for such scaling down within the present project. However, we can mention that much research is being devoted to the development of reformers for small-scale local production of hydrogen. Hydrogen is costly to transport, and therefore local or on-site production is seen as an important stepping-stone technology in the transition to hydrogen-based infrastructure (Schjølberg et al., 2012).

The technologies in the field are developing rapidly, and with the scope of this report we could not make a complete review of all existing and developing technologies. Future research could include studying the development of small-scale reformers for biogas applications, as well as novel technologies such as plasma reformers. When evaluating the different technologies, scalability and costs are vital. Scalability and cost analyses would be a logical continuation to the present project, since they could not be included here due to the limited scope. Another interesting continuation of this project would be a more detailed study of energy balances and greenhouse gases for the different technical pathways, where the whole life cycle, including cultivation of feedstock, is included. Extending the system boundary to include production of biofuel would also be interesting, as it would enable comparison with other types of biofuels.

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