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Biogenic carbon dioxide as feedstock for production of chemicals and fuels

A techno-economic assessment with a European perspective

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Preface

This report was mainly financed by the EnCO2re flagship programme “Medium and long-term perspective of markets for innovative CO_2 utilisation” within climate-KIC. The report also benefited from research undertaken in the research project Sustainable Plastics and Transition Pathways (STEPS) financed by Mistra. The author would like to thank Stefan Lechtenböhmer, Lars J Nilsson, Ellen Palm and Valentin Vogl for their helpful comments on an earlier draft of this report.

Summary

The use of fossil resources must be phased out during the next few decades in order to meet the adopted 2° target. The transition to non-fossil feedstocks in the production of chemicals and transportation fuels will make it increasingly important to economise on the biomass carbon since biomass is a limited resource. Carbon dioxide (CO_2) can be used as carbon feedstock and thus serve as a valuable complement to biomass. CO_2 can be transformed into various chemicals via reaction with hydrogen, which can be produced from electricity and water.

The objectives of this report are to technically and economically assess the opportunities to produce chemicals and fuels based on electricity and biogenic CO_2 from different biomass conversion processes in Europe and to identify promising production process routes. The report focuses on the production of methanol and methane, which are widely used in the chemical industry and as fuel.

The total generation of CO_2 from the current centralised use of biomass and wastes in Europe is estimated to 395 Mt CO_2. Most of this CO_2 originates from biomass combustion (287 Mt) and waste incineration (81 Mt) and less from biogas production (23 Mt) and ethanol production (4.4 Mt). The technical potential production of chemicals based on this amount of biogenic CO_2 is estimated to 6.2 EJ of methane (about one third of the current use of fossil methane in Europe), assuming all the CO_2 is converted into methane, or alternatively to a combination of 4.6 EJ of methanol (about five times the current use of methanol in Europe) and 0.4 EJ of methane. The production is estimated to require 2500-3200 TWh of electricity, depending on transformation product. Hence, the use of biogenic CO_2 and electricity increases the potential production of chemicals and fuels from non-fossil resources substantially, but implies an enormous expansion of renewable electricity production in order to supply the required volume of low-carbon electricity.

The main cost driver for CO_2 utilisation is the cost of electrolysis, which is largely independent of the biomass conversion process. The cost of electrolysis is dominated by the cost of electricity if the electrolyser is operated with high capacity factor. A low capacity factor makes the capital cost the main cost driver. The cost of CO_2 capture is the second most important cost driver for the utilisation of CO_2 from biomass combustion and something that makes this route more costly than others. The production cost of methanol from biogenic CO_2 in flue gases is calculated to about €780/t methanol in this report when including the main process steps and assuming an electricity price of €50/MWh. The production of methanol from CO_2 and electricity can under most circumstances not meet the current market price of methanol, which is set by the production based on natural gas or other fossil feedstocks. The competitiveness of CO_2-based methanol and methane is thus largely dependent on the cost relation between electricity and fossil feedstocks. Future technical development of electrolysis and the adoption of climate policies which reduce the cost of electricity in relation to fossil feedstocks would improve the competitiveness of CO_2-based chemicals and fuels.

The most promising process routes in the short-term perspective are to utilise CO_2 from anaerobic digestion and fermentation for production of methane or methanol. A major strength of these routes is the high technical readiness. Currently, biomass combustion generates the largest volumes of biogenic CO_2. The technical readiness is, however, lower for utilising this CO_2 than for the previously mentioned options. The large investments required for post CO_2 separation or oxyfuel combustion also pose a barrier. Biomass gasification with integrated CO_2 utilisation is the most promising option for the medium term assuming biomass gasification can overcome its technical and economic or barriers and reach commercial scale. This route does not require CO_2 separation and offers high technical potential since the technology is compatible with most biomass feedstocks.

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Contents

1 Introduction

The bulk of the European and global production of liquid and gaseous fuels, chemicals and plastics is derived from fossil resources. In the long-term, the use of fossil resources will have to be phased out in order to meet the adopted 2°C climate target, which implies that the greenhouse gas emissions (GHG) must decrease to or below zero before 2100 (UNFCC, 2015). Today, a small proportion of chemicals, plastics and liquid and gaseous fuels is produced from non-fossil resources, primarily biomass. Bio-based plastics accounted for only about 1% of the global plastics production in 2016 (European Bioplastics, 2017). Biofuels accounted for 6 and 1%, respectively, of the global production and use of liquid and gaseous fuels in 2014 (IEA, 2016).

The EU and many of its member states have an ambition to develop the use of biomass and their bio-based economies further (see e.g. European Commission, 2011 and 2012). The extent to which the use of biomass can be expanded is, however, limited by ecological restrictions and land-use competition. Most European and global resource assessments indicate that the potential biomass supply is considerably smaller than the current use of fossil resources (see e.g. EEA, 2006; Ericsson and Nilsson, 2006; IPCC, 2014). It is therefore important to curb the demand for liquid and gaseous carbon-containing fuels and to develop other renewable energy sources and feedstocks that can serve as complement to biomass. One option is to use carbon dioxide (CO_2) as feedstock for production of chemicals, plastics and fuels (Quadrelli et al., 2011; Palm et al., 2016). CO_2 is in fact already used as feedstock in certain industrial processes such as the production of urea, salicylic acid and carbonates, but the CO_2 consumption in these applications is fairly limited (Quadrelli et al., 2011).

The use of CO_2 as feedstock, sometimes referred to as carbon capture and utilisation (CCU), is attracting a growing interest around the world since it can save natural resources and reduce or delay CO_2 emissions (see e.g. Quadrelli et al., 2015). CO_2 can be transformed into various bulk chemicals via hydrogenation, i.e. reaction with hydrogen. Hydrogen can be produced from water via electrolysis, a process that may require large amounts of electricity. The climate benefit of using CO_2 as feedstock is thus conditioned by the use of electricity with low GHG emissions. Fossil fuels still make an important contribution to electricity supply in many European countries, but the electricity sector is experiencing a strong development towards higher proportions of renewable energy sources and lower GHG emissions (IEA, 2016). This development makes electricity a more attractive energy carrier (and thus CCU more interesting). Another aspect of this development is the growing use of electricity from variable renewable energy sources, mainly wind and solar energy, a development that calls for increased flexibility in other parts of the energy system. One flexibility measure that is attracting much attention is power-to-gas (see eg. Götz et al., 2016). This technology involves the production of hydrogen from (variable) electricity via dynamic operation of an electrolyser. Since hydrogen is difficult to store and distribute, methane is generally the preferred gaseous product, but this requires access to a carbon source such as CO_2. CO_2 and hydrogen can also be used as feedstock for production of various other chemicals and fuels.

Many biomass conversion processes generate CO_2 and they are attractive carbon sources due to the biogenic origin and since some of the conversion processes generate gaseous streams with high CO_2 concentration. There are a number of technical and economic analyses that address the utilisation of biogenic CO_2 from anaerobic digestion (see e.g. Benjaminsson et al., 2013; Luo et al., 2012), thermal gasification or both (see e.g. Mohseni et al., 2012; Götz et al., 2016). The opportunity to utilise biogenic CO_2 is also recognised by Connelly et al. (2014) who have made a comparative assessment of different renewable transportation fuels, including fuels produced from biomass, electricity and CO_2 (from biomass conversion or air capture) in the context of a 100% renewable energy system. Their conclusion is that direct electrification is the preferable option and that liquid and gaseous transportation fuels from electricity, biomass and CO_2 is a valuable complement for the parts of the transportation sector that are difficult to electrify. This report focuses on biogenic CO_2 and investigates the opportunity to utilise CO_2 from different biomass conversion processes and electricity for the production of chemicals and fuels in a European context. The studied biomass conversion processes include (centralised) combustion, waste incineration, anaerobic digestion, fermentation and thermal gasification. Thermal gasification is not used at commercial scale today, but it is highly relevant due to its large technical potential. The opportunity to utilise biogenic CO_2 from these processes and the technical options for doing so differ in several respects.

The objectives of this report are to technically and economically assess the opportunities to produce chemicals and fuels based on electricity and biogenic CO_2 from different biomass conversion processes in Europe and to identify promising production process routes.

The report addresses the following questions:

- Which are the key processes and technologies for utilisation of biogenic CO_2 and what are their main characteristics?
- How much biogenic CO_2 is currently generated, or could be generated in the future, from different biomass conversion processes in Europe?
- How much chemicals can be produced from the biogenic CO_2 that is available in Europe today and how much electricity would be required?
- What are the main cost drivers of utilising CO_2 from different biomass conversion processes and what are the production costs of CO_2-based chemicals?
- Which are the most promising process routes in the short and long-term?

The report is organised as follow: it presents an overview of the current European biomass use and conversion technologies; describes the key technologies and processes that enables the production of chemicals and fuels from electricity and biogenic CO_2 from different conversion processes; provides a techno-economic assessment of different process routes; and ends with a concluding discussion.

2 Bioenergy - Use, conversion technologies and CO_2 generation

This chapter provides an overview of the current energetic use of biomass in Europe and of the used conversion technologies and their characteristics. It also presents CO_2 generation factors for different types of biomass and conversion processes.

2.1 Total biomass use

The use of biomass and renewable municipal waste in OECD Europe has more than doubled since 1990 and amounted to about 5.6 EJ in 2015 (IEA, 2016). Biomass is the main renewable energy source in Europe and accounted for almost 8% of the primary energy supply in this region (Figure 1). The use of biomass is dominated by solid biofuels, but the proportions of renewable municipal waste, biogas and liquid biofuels have increased since 1990. The solid biofuels and most of the biogas are used in heat and electricity production while the liquid biofuels and some of the biogas are used as transportation fuels. Electricity production from biomass and renewable waste in OECD Europe in 2015 amounted to 174 TWh, accounting for about 14% of total electricity production (IEA, 2016). The consumption of liquid and gaseous biofuels in the transportation sector in 2014[1] amounted to 587 PJ, corresponding to about 5% of the energy use in road transportation (IEA, 2016).

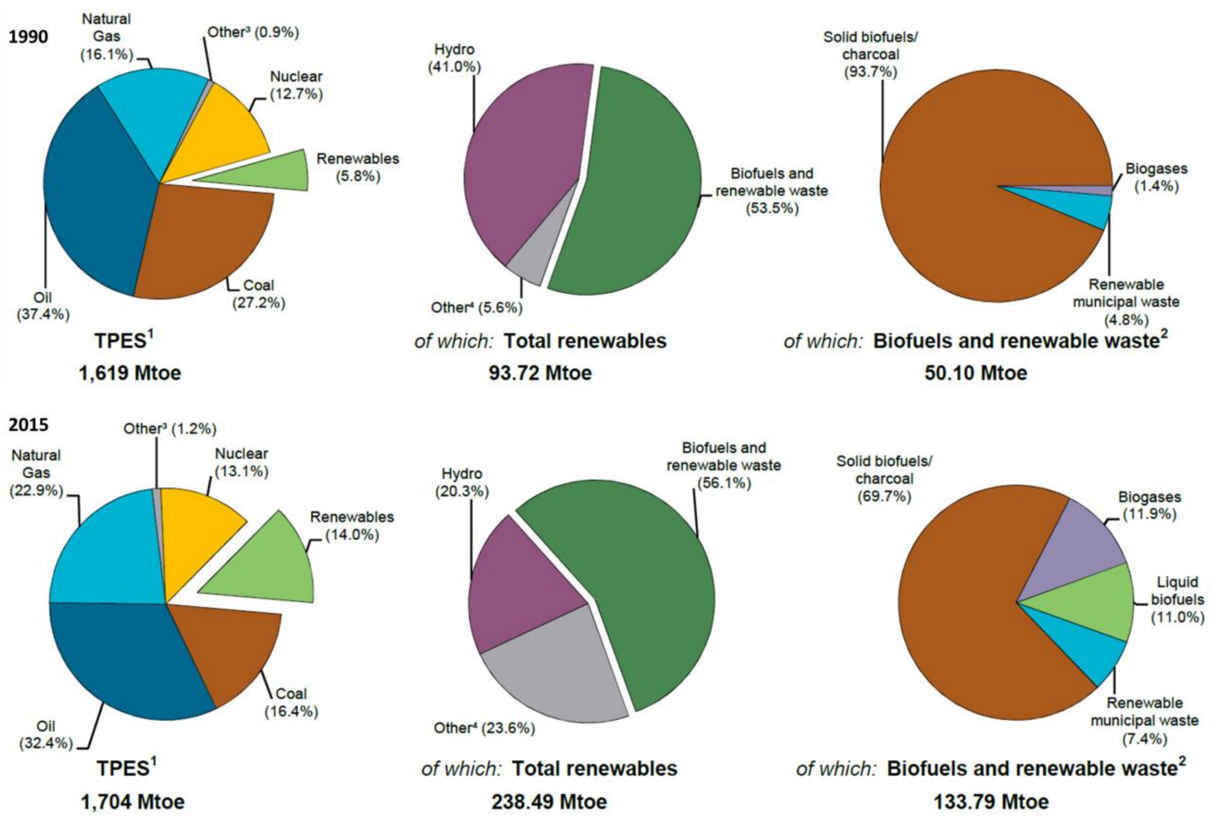

Figure 1: The pie charts illustrate the distribution of energy sources in total primary energy supply (TPES), among renewable energy sources and among biofuels and renewable waste in OECD Europe in 1990 (above) and 2015 (below) (IEA, 2016). Total use of biofuels and renewable waste amounted to 2098 PJ in 1990 and 5602 PJ in 2015.

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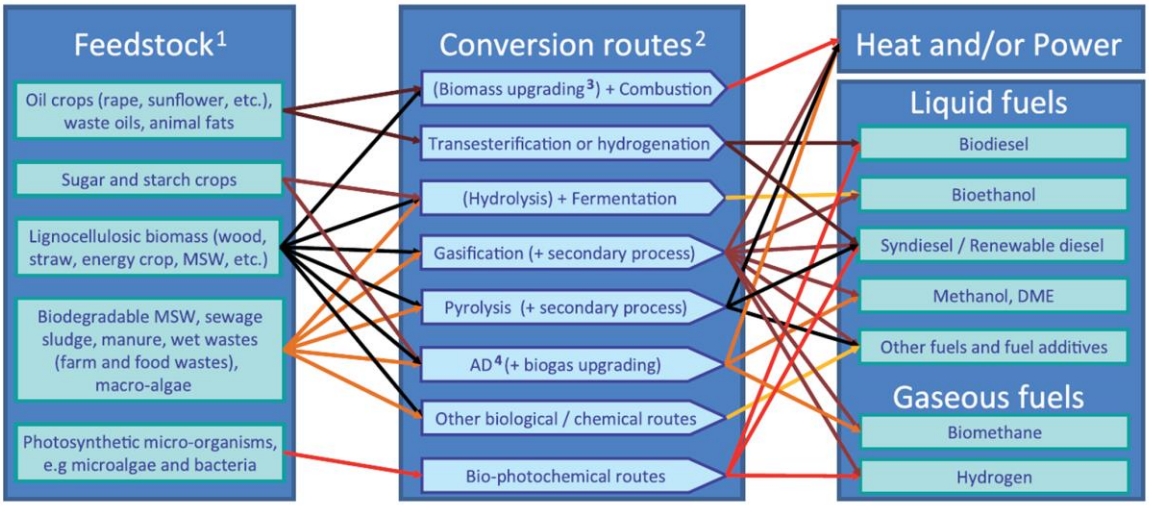
[1] This data is only available for 2014 and earlier.

2.2 Biomass conversion processes

The biomass use in the EU involves the conversion of biomass to heat, electricity and different liquid and gaseous fuels via a number of conversion processes. Final energy use of biomass often consists of combustion (in boilers, stoves, engines, etc)[2], a process that generates CO_2 in the flue gases. However, in order to make biomass a more practical fuel or enable combustion in for example vehicle engines, the biomass must first be converted to a liquid or gaseous fuel via for example anaerobic digestion or fermentation, processes that also generate CO_2.

Figure 2 illustrates different bioenergy routes where biomass is converted to heat, electricity and different liquid and gaseous chemicals/fuels via a number of conversion processes. The conversion processes that are widely used today include combustion, anaerobic digestion and biodiesel production via transesterification or hydrogenation of vegetable oils while the others are at research or demonstration stage. Some conversion processes require specific biomass raw materials while others are compatible with most raw materials. Sections 2.2.1-2.2.4 describe the biomass conversion processes that are most relevant with regard to potential CO_2 utilisation, namely biomass combustion (and waste incineration) within central transformation (i.e. industrial, district heat, CHP and power plants), anaerobic digestion, fermentation and thermal gasification.



[1] Parts of each feedstock, e.g. crop residues, could also be used in other routes

[2] Each route also gives co-products

[3] Biomass upgrading includes any one of the densification processes (pelletisation, pyrolysis, torrefaction, etc.)

[4] AD = Anaerobic Digestion

Figure 2: Schematic view of different bioenergy routes (Bauen et al., 2009). The generation of CO_2 is not included in this figure.

2.2.1 Biomass combustion and waste incineration

Biomass combustion and waste incineration are processes that release heat and generate CO_2 and water which are found in the flue gases. The released heat is used for production of electricity,

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[2] In the case of hydrogen and syngas from biomass, final energy use could also be electrochemical conversion to electricity in a fuel cell.

process heat and district heat. Biomass is also combusted in small-scale applications for providing space heating and hot tap water, but these applications are not suitable for CO_2 utilisation.

In 2014, 2870 PJ[3] of biomass was combusted for production of electricity, district heat and process heat in OECD Europe. This biomass consisted mainly of solid biofuels[4] (1936 PJ), but also of biogas (520 PJ) and of renewable municipal waste (414 PJ) (IEA, 2016). The biomass use was divided between the transformation sector (2030 PJ) and industry (840 PJ). The transformation sector encompasses the combustion of biomass in district heat, CHP and power plants, as well as the combustion of renewable and non-renewable waste in waste incineration plants with energy recovery. The forest industry is an important industrial user of biomass energy; the processing of wood for production of sawn wood and pulp (for production of paper) generates large amounts of by-products that are combusted internally for production of process heat and electricity.

The combustion of non-renewable municipal waste and industrial waste amounted to 400 PJ and 166 PJ, respectively in 2014 (IEA, 2016). The non-renewable waste is combusted in waste incineration plants in the transformation sector. The industrial waste is combusted in the transformation sector as well as in industry.

Combustion processes are well understood and a wide range of existing commercial technologies are tailored to the characteristics of the biomass and the scale of their application. The largest dedicated biomass combustion plants have a thermal capacity of around 500 MW. Biomass is sometimes also co-fired with coal in large (> 500 MW) power plants.

2.2.2 Anaerobic digestion

Anaerobic digestion is a complex series of reactions where organic material is degraded by microorganisms in the absence of oxygen. The process generates biogas, which is a mixture of methane (50-70%) and CO_2, and a residual, biodigestate, that may be used as fertiliser.

The biogas production in Europe in 2014 was estimated to 630 PJ (IEA, 2016). Around 80% of the biogas was produced from sewage sludge, food-processing waste, household waste, agricultural waste and energy crops such as maize and lay crops (EurObserv'ER, 2015). The remaining 20% of the biogas was captured from landfills. Germany accounted for about half of the European biogas production and also stands out in its large use of energy crops for production of biogas (ibid).

At the end of 2014 more than 17,000 biogas production plants were in operation in Europe (EBA, 2016). The biogas produced in Europe is mainly used locally for CHP production; the focus is often on electricity production since the demand for heat is often low unless the plant is connected to a district heating network. A fairly small, but growing, volume of biogas is upgraded to biomethane with the quality of natural gas in order to be injected in the gas grid or to be used locally as vehicle fuel. In 2014 upgrading technology was installed at 367 biogas plants in Europe with a total capacity to upgrade about 60 PJ of biogas per year (EBA, 2016). Only about 6 PJ of biomethane, i.e. less than 1% of the total biogas production, was used as vehicle fuel (two thirds of which was used in Sweden) (EurObserv'ER, 2015).

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[3] This value excludes the use of 1750 PJ of biomass that is used in buildings for heating purposes.

[4] Solid biofuels include wood waste and other solid biomass, but also black liquor, a lignin-containing by-product from pulp production.

Anaerobic digestion is considered to be a mature technology, but with ongoing development efforts into increasing the biogas yield, digestion of cellulosic biomass and upgrading technologies. Biogas production plants are generally in the scale of 1-10 MW of biogas produced. The size of these plants is restricted by the local availability of substrates since the energy content of substrates is fairly small, thus making long transportation of the substrates uneconomical.

2.2.3 Fermentation

Fermentation of biomass involves the decomposition of sugar to acids, alcohol and gases (mainly CO_2) by microorganisms such as yeasts under low or no presence of oxygen. Biomass fermentation is currently mainly used for production of ethanol, a process that generates a very concentrated CO_2 stream (99% CO_2). Other commercial products from biomass fermentation include lactic acid, polyhydroxyalkanoates and 1,3 propanediol (Gessen-Gondelac et al., 2014).

The renewable ethanol production in Europe[5] amounted to 5.8 billion litres (121 PJ) in 2015, of which 4.5 billion litres was used as fuel, 0.8 billion litres was used in industry and 0.4 billion litres was used for production of food and beverages (ePURE 2016). In industry, ethanol is mainly used as solvent, antifreeze and as feedstock for production of bio-ethylene, which is used in the production of bio-polyethylene, a bioplastic. Most of the ethanol was produced from wheat, maize and sugar beets while cellulosic biomass made a marginal contribution (about 3%) (ePURE, 2016). The ethanol production from sugar and starch yields a co-product, distillers grain, nearly all of which is used as animal feed.

There were 99 facilities producing renewable ethanol for fuel or industrial purposes in Europe in 2014 (ePURE, 2015). These facilities are spread over many countries, but most of the installed capacity is located in France and Germany.

The production of ethanol via fermentation of sugar and starch rich crops has been applied at industrial scale for many decades and involves mature technologies. The use of cellulosic biomass for production of ethanol involves a more complex and less mature process since the biomass needs to be pretreated and hydrolysed (with acids or enzymes) prior to fermentation.

In 2015, about 0.4 million tonnes of CO_2 was recovered from renewable ethanol production in Europe (ePURE, 2016). The main market for this CO_2 is the beverage and food industry where it is used in carbonated beverages and for refrigeration and quick freezing. Some of the CO_2 is also sold to the chemical industry, mainly for production of urea (Xu et al., 2010). In the US and Canada a handful of ethanol production plants are currently capturing CO_2 to be used for enhanced oil recovery (Kemper, 2015).

2.2.4 Thermal gasification

Biomass gasification is a process where biomass is converted to a mixture of carbon monoxide (CO), CO_2, hydrogen and methane - commonly referred to as producer gas - by heating it in the presence of limited oxygen. The composition of the gas mixture varies depending on the type of biomass and the gasification technology and medium, which in turn are often dictated by the intended final product. The producer gas may be used for heat and electricity production in boilers and gas engines or upgraded to a higher quality gas mixture, syngas, a process that releases CO_2. The syngas can be used in fuel and chemical synthesis or in electricity generation in a gas turbine.

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[5] The member companies of ePURE are found in the EU and account for 90% of the installed renewable ethanol production capacity in this region.

Gasification of biomass has been possible for much of the last century but the technology is still largely at demonstration stage. There are currently about 20-30 biomass gasification demonstration plants in Europe and a handful outside of Europe (Molino et al., 2016; IEA, 2017). Most of the demonstration plants involve CHP production. However, the demonstration plant Gobigas[6] in Gothenburg, Sweden, produces methane (20 MW) for the (natural) gas grid. Chemical synthesis is also being tested in smaller pilot plants that are incorporated into demonstration plants for biomass gasification and CHP production (IEA, 2017).

There are three main categories of gasifiers: fixed bed gasifier, fluidised bed gasifiers and entrained flow gasifiers. The gasification medium is oxygen, air or steam. The biomass often needs to be pre-treated prior to the gasification and the producer gas usually needs to be cleaned in order to remove impurities and conditioned in order to adjust the CO/H_2 ratio before synthesis. The formation of tars[7] during gasification may be considered the Achilles heel of biomass gasification since the tars may cause catalyst poisoning in the downstream chemical synthesis (Molino et al., 2016). The removal of tars is therefore the greatest technical challenge to overcome in order to develop successful utilisation of biomass derived producer gas or syngas (Molino et al., 2016).

A key advantage of the gasification pathway is that it can convert all of the organic matter in biomass into producer gas. In particular, the lignin component of biomass which enzymes/microorganisms can hardly crack is readily gasified and made available for fuel and chemical production. Hence, thermal gasification provides an opportunity to produce chemicals and fuels from a broad range of biomass feedstocks and waste, including e.g. forestry and agricultural residues, black liquor and municipal waste.

2.3 CO_2 generation factors

The studied biomass conversion processes generate biogenic CO_2 that today are either vented to the air or released via the flue gases. At present, CO_2 is only captured from certain ethanol production plants. The concentration of CO_2 in CO_2 containing gases varies greatly between different processes, being about 99% in the gases from fermentation, 30-50% in biogas and 10-15% in the flue gases from biomass combustion.

The CO_2 emission factor for combustion of biomass and waste varies between different types of biomass and wastes depending on their chemical composition (carbon content). Table 1 lists the default CO_2 emission factors from the 2006 IPCC guidelines. The CO_2 emission factors for different solid biofuels can be approximated to about 100 kg CO_2/GJ.

The CO_2 generation in anaerobic digestion was calculated to 37 kg CO_2/GJ biogas[8] assuming the biogas consists of 60% methane and 40% CO_2 by volume. All the energy content in biogas lies in the methane. The CO_2 generation in ethanol production via fermentation is assumed to be 0.76 t CO_2/m^3 based on Xu et al. (2010).

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[6] Gobigas involves a circulating fluidised bed (CFB) steam gasifier and methanation unit which have been in operation since 2013.

[7] Tars include all the organic compounds that are present in the syngas, excluding hydrocarbons from C1 to C6 (i.e. methane up to hexane) (Molino et al., 2016).

[8] CO_2 content [kg/MJ biogas] = (0.4 × 44) ÷ (0.6 × 800), where the values refer to the molar mass of CO_2 (44 g/mol) and molar energy of methane (800 kJ/mol).

Table 1: Default CO_2 emission factors for stationary combustion of different biomass and waste fuels based on the IPCC guidelines (IPCC, 2006).

Fuel	**CO_2 emission factor kg CO_2/GJ (LHV)**
Wood/wood waste	112
Other solid biomass	100
Black liquor	95
Biogas	55
Renewable municipal waste	100
Non-renewable municipal waste	92
Industrial waste	143

3 Key processes and technologies for CO_2 utilisation

This chapter describes a number of key processes and technologies that enable the production of chemicals and fuels from electricity and CO_2 from different biomass conversion processes (but also from other sources.

Figure 3 illustrates possible process routes for producing various chemicals and fuels from electricity and biomass, including the CO_2 generated in different biomass conversion processes. The figure does not include all possible routes and transformation products of CO_2, but rather focuses on important routes and products that have synergies with the biomass conversion routes that today are in use or at demonstration stage. Many of the routes involve methanol and methane as intermediate or final product. These compounds are interesting since methane is the main product of anaerobic digestion and due to their simple molecular structures; methane is the simplest hydrocarbon and methanol the simplest liquid compound and alcohol containing only one carbon. Both are widely used today as fuel and chemical intermediates (see Box 1).

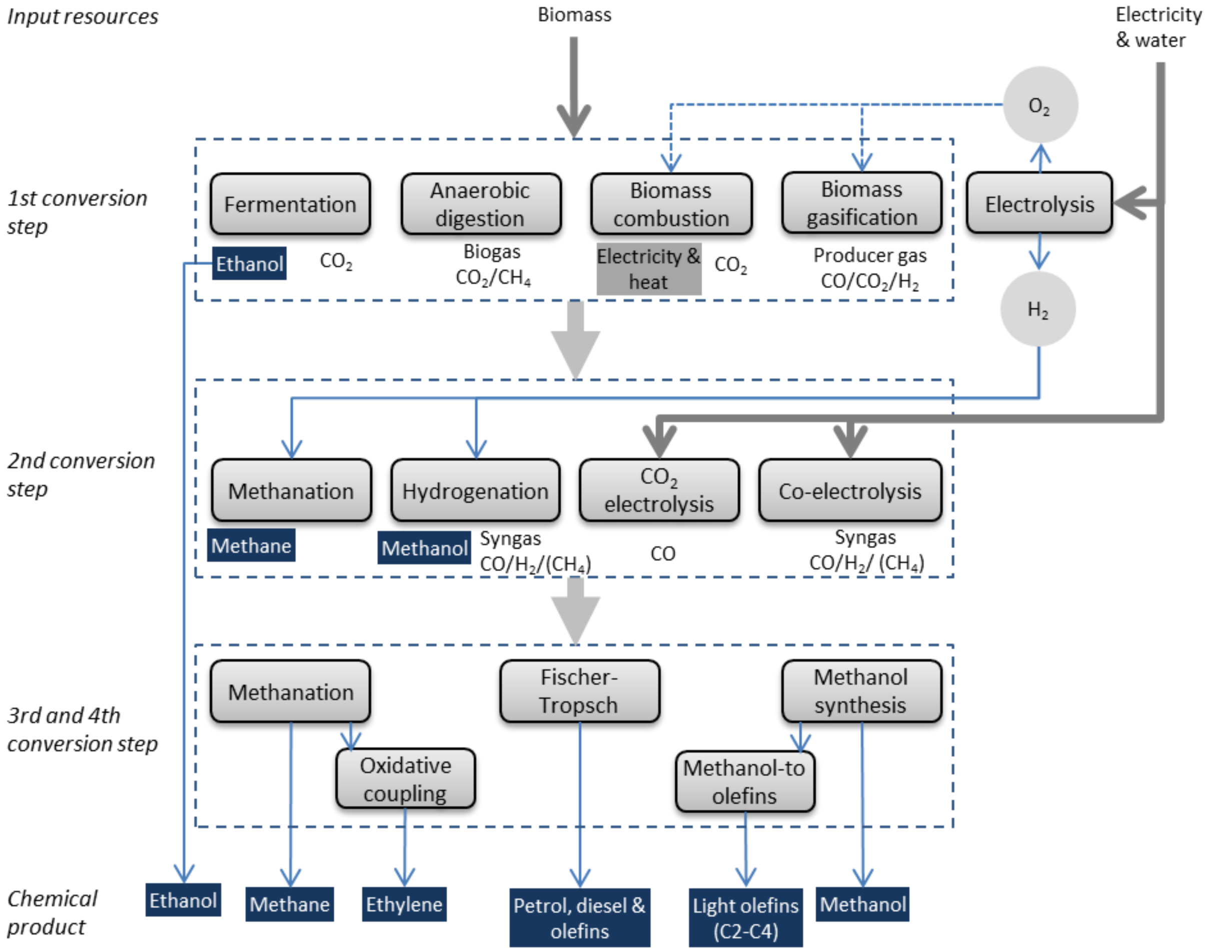

Figure 3: Important possible production routes for the production of chemicals and fuels from electricity and biomass, including the biogenic CO_2. In the second conversion step, CO_2 electrolysis requires CO_2 as input whereas the other three processes can use CO_2, biogas or producer gas as input. In the third conversion step, syngas or a mixture of syngas and methane can be used in methanation whereas the other two processes require syngas. The figure only includes to ethanol as fermentation product and does not illustrate the possibility to convert this to ethylene etc.

Box 1: Methane and methanol

Methane is the main component in natural gas which essentially is fossil methane. Methane is also produced via anaerobic digestion and is then called biogas. Total supply of natural gas in Europe amounted to 17,400 PJ and the supply of biogas amounted to 630 PJ (IEA, 2016). Methane is an important energy carrier in Europe and worldwide; it is primarily used for production of electricity and heat, but also as transportation fuel. Methane is also an important feedstock in the chemical industry, primarily by being the main feedstock for production of hydrogen and syngas which are used for production of ammonia, various refinery products, methanol etc. Most of Europe host extensive distribution networks for methane. Methane is also imported and distributed in liquid form.

Methanol is an important chemical feedstock; the main chemical derivatives are formaldehyde, light olefins, ascetic acid, methyl tertiary-butyl ether (MTBE) and dimethyl ether (DME). The transformation into light olefins (methanol-to-olefins, MTO) is a rapidly growing sector, now being the second most important end use for methanol worldwide (Alvarado, 2016a). Historically, there has been little direct use of methanol as transportation fuel, but this is changing due to the blending of methanol in petrol in China. In Europe, methanol is mainly used indirectly as transportation fuel via its use as feedstock in transesterification of vegetable oils for production of biodiesel (Pérez-Fortes et al., 2015).

Methanol is typically produced from syngas derived from natural gas, coal or residual oil. Globally, natural gas is the most important raw material, but coal is becoming an increasingly important raw material in China and now represents around 35% of installed global capacity (Alvarado, 2016b). The European methanol consumption amounted to about 7.6 Mt (2.9 Mt imported) in 2013 (Pérez-Fortes et al., 2015).

3.1 CO_2 capture and separation

3.1.1 Overview

The composition of CO_2 containing gas streams varies considerably, even within similar processes. Apart from CO_2, the gas streams may contain nitrogen, water vapour, hydrogen sulphide, CO, particular matter, unburnt hydrocarbons, SOx and NOx. Gas cleaning and separation is normally required in order to produce CO_2 of an appropriate quality to be used in the production of fuels and chemicals. However, the specific requirements of the cleaning and separation vary greatly depending on the composition of the gas stream and the downstream process. Processes that involve catalysts are normally very sensitive to impurities which can poison and deactivate the catalyst. CO_2 separation and gas cleaning are required for utilisation of the CO_2 in flue gases from combustion. For the almost pure CO_2 gas stream from fermentation, on the other hand, the procedure is simple; only condensation of water vapour is required. CO_2 separation is also not necessary for utilisation of the CO_2 in biogas and producer gas, but limits the transformation product to methane in the case of biogas. The biogas and producer gas must, however, normally undergo desulphurisation, and in the case of producer gas also other cleaning processes before chemical synthesis.

The maturity of different CO_2 separation technologies varies considerably between different applications. CO_2 separation technologies are well-established and currently applied for purification of certain industrial gas streams (see Section 3.1.2) while CO_2 capture from combustion systems is at demonstration stage (IEA, 2012). The demonstration plants for CO_2

capture involve fossil fuel fired combustion plants. CO_2 capture has so far not been demonstrated at dedicated biomass combustion plants, but the technical maturity is considered to be largely the same as for fossil fuel combustion (Kemper, 2015).

3.1.2 CO_2 capture processes and systems

The CO_2 capture processes and systems can be divided into post combustion, oxyfuel, pre-combustion and industrial processes (Figure 4). All processes and systems involve the separation of CO_2, hydrogen or oxygen from a bulk gas stream (such as flue gas, producer gas, air, raw natural gas and biogas). The separation can be accomplished by means of physical or chemical solvents, membranes, solid sorbents, cryogenic separation, or by a combination of these methods. The majority of CO_2 separation in commercial use today involves physical and chemical absorption in liquids (Styring, 2015).

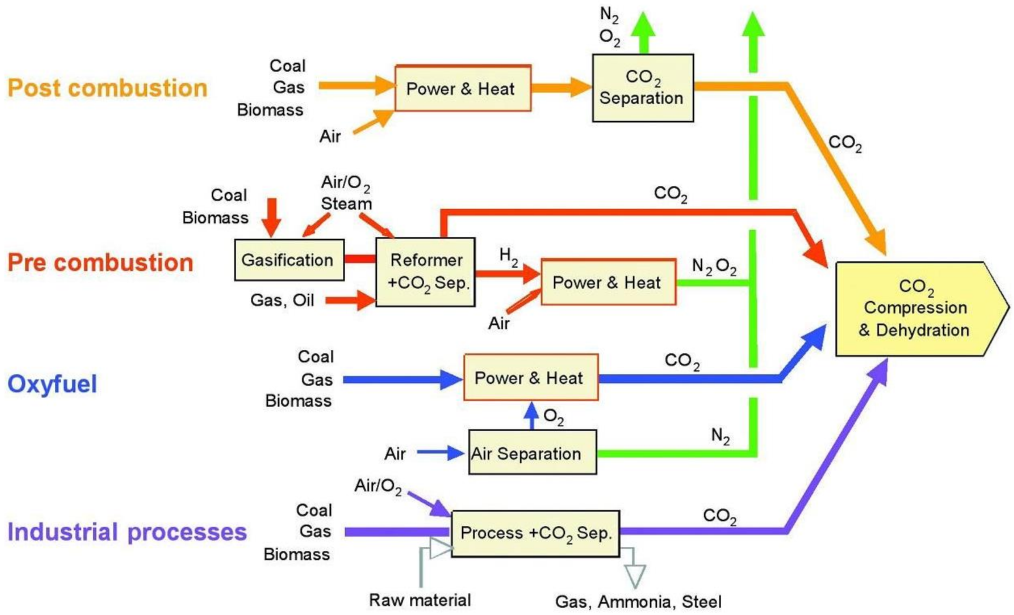

Figure 4: Overview of CO_2 capture processes and systems (IPCC, 2005).

Post combustion systems separate CO_2 from the flue gases produced by the combustion of the primary fuel in air. Due to the low concentration of CO_2 in the flue gas (4-14%), the systems involve the handling of large volumes of gas. This results in large equipment sizes and high capital costs. Chemical absorption using an amine is the most mature and reliable technology for post combustion CO_2 removal although this technology has not been applied on flue gases at commercial scale (Mondal et al., 2012). The flue gases should be cleaned prior to CO_2 separation. Post combustion and combustion systems for power plants can capture 85-95% of the CO_2 in the flue gas (IPCC, 2005). Chemical absorption requires high amounts of energy, especially heat, for regeneration of the amine. This method involves a heat demand of 2.7-3.3 GJ/tCO_2 captured and an electricity demand of 0.06-0.11 GJ/tCO_2 (IPCC, 2005). The high energy requirements, amine degradation and high equipment corrosion rate are the main drawbacks of this technology and something that makes the development of new solvents a technical priority (Mondal et al., 2012).

Pre-combustion systems involve thermal gasification of the primary fuel in a reactor with steam, air or oxygen to produce a gas mixture (producer gas or syngas) consisting mainly of CO and hydrogen. The gas mixture is then reacted with steam in a water gas shift reactor in order to adjust the CO/H_2 ratio. This increases the CO_2 content in the resulting gas to 15-60% (by volume on dry basis) (IPCC, 2005). The CO_2 separation can be carried with a physical solvent such as Rectisol or Selexol [9] which are available at low cost (Mondal et al., 2012). The pre-combustion system would typically be used in combination with integrated gasification combined cycle (IGCC) technology at a power or CHP plant or with gasification technology followed by chemical synthesis. The energy requirement for CO_2 separation and compression could be about half of that required for post combustion capture (Mondal et al., 2012). On the other hand, this concept requires a "chemical plant" (gasification reactor and cleaning processes) in front of the gas turbine which makes the operation of the turbine less flexible and increases the risk for shutdown (Mondal et al., 2012).

Oxyfuel combustion systems use oxygen instead of air for combustion of the primary fuel to produce a flue gas that mainly contains CO_2 and water vapour. The water vapour is easily removed by condensation which leaves a dry flue gas with a CO_2 content of 70-95 % depending on the use of excess oxygen etc. The remaining CO_2 can be purified at relatively low cost, for example using cryogenic separation (Mondal et al., 2012). The most frequently proposed version of oxyfuel combustion uses a cryogenic air separation unit for the supply of oxygen. The oxygen is mixed with recycled flue gases either prior to combustion or in the combustion chamber in order to keep the temperature at an acceptable level (Mondal et al., 2012). The oxygen can, however, also be supplied from an electrolyser assuming there is demand for hydrogen in other process units at the site. The cost of CO_2 capture is lower for this concept than for post combustion, but the cost of air separation and flue gas recirculation reduces the economic benefit (ibid).

CO_2 capture can also be applied in various *industrial processes* and is used today in several industrial applications. Important examples are the large-scale production of hydrogen at ammonia and fertiliser production plants and petroleum refineries which relies on CO_2 capture technologies that could also be used for pre-combustion capture (IPCC, 2005). CO_2 capture is also used for separation of CO_2 from raw natural gas; the technologies in this case are similar to those suitable for post-combustion capture (ibid). Furthermore, CO_2 separation is applied in numerous biogas upgrading plants. The dominating technologies for this are water scrubbing (physical absorption), chemical absorption and pressure swing adsorption (PSA). A small number of biogas plants apply cryogenic separation. This upgrading technology involves high pressures and thus requires a large amount of energy, accounting for 5-10% of the biomethane produced. The advantage of this technology is that it produces liquid and high purity biomethane (Sun et al., 2015).

3.2 Hydrogen production via electrolysis and hydrogen storage

Electrolysis offers a means of producing hydrogen from water via energy input, mainly electricity. By deploying a direct current to water that is placed in an electrochemical cell, water is dissociated into hydrogen and oxygen (R1).

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \qquad \text{(R1)}$$

The electrochemical reaction is endothermic and requires high input of electricity. The electrolyser efficiency represents the total energy-to-fuel (hydrogen) efficiency of the electrolyser system and is usually calculated based on lower heating values (LHV). The theoretical maximum efficiency of electrolysis is 85 % (LHV). The electricity-to-hydrogen efficiency can be higher for

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[9] Rectisol and Selexol are trade names for organic solvents that are used for removal of acid gases. Rectisol mainly contains methanol and Selexol contains DME and propyleneglycol.

high-temperature electrolysis if the heat is supplied from "waste heat" at the site. Apart from hydrogen, water electrolysis produces 66 kg oxygen per GJ of hydrogen (see appendix).

There are three main technologies for water electrolysis that are in different stages of development: alkaline electrolysis, proton exchange membrane (PEM) electrolysis and solid oxide electrolysis cells (SOEC). These technologies are described in Sections 3.2.1-3.2.3 and their characteristics are summarised in Table 2. Electrolysis may also be used for dissociation of CO_2 (see Section 3.3.4).

Electrolysis is the reverse process of that in a fuel cell which combines hydrogen and oxygen to produce electricity and water. For each electrolysis technology, there is a corresponding fuel cell, i.e. the alkaline FC, PEM FC and SOFC.

Table 2: Summary of the main characteristics of different technologies for water electrolysis (Mathiesen et al., 2013).

	Alkaline cell	**PEM cell**	**SOEC**
Operational temperature (°C)	70-100	50-80	700-1000
Energy-to-hydrogen efficiency (LHV)	50-70%	68-72%	77%
Stage of development	Commercial scale, widely spread	Commercial	Laboratory
Economics 2012 -CAPEX (M€/MW) -O&M cost (% of CAPEX/yr)	 1.07 4	 2.55 4	 - -
Economics 2020-2030 -CAPEX (M€/MW) -O&M cost (% of CAPEX/yr)	 0.87 4	 1.27 4	 0.93-0.35 3
Strengths	Proven and robust technology, cheapest today	Fast cold start and high flexibility, simple compact design.	Potentially highest efficiency and lowest cost in the future.
Weaknesses	High maintenance cost (corrosive electrolyte)	High material cost, limited lifetime	The long-term durability of the cells needs to be proven. Less flexible (slow cold start).

3.2.1 Alkaline electrolysis

Alkaline electrolysis is the dominant technology for water electrolysis and has been commercially available at MW scale for decades (Götz et al., 2016). Alkaline electrolysis uses an alkaline solution generally containing potassium hydroxide as electrolyte and the electrodes consist of nickel plated steel (anode) and steel (cathode) (Graves et al., 2011). State-of-the-art alkaline electrolysis is carried out under low temperature (70-100°C) and atmospheric pressure. The efficiency of alkaline electrolysers in operation today varies greatly and is often quite low (40-70%) since these units are typically not operated to maximise energy efficiency, but rather economic efficiency (Mathiesen et al., 2013).

Alkaline electrolysers rely on mature and robust technology and are currently cheaper than other technologies. The lifetime of alkaline cells is long compared to other types of cells, up to 30 years, but the cells need major service every six years due to the highly corrosive electrolyte (Mathiesen et al., 2013). The technology has been developed for continuous stable operation, but it can also be operated under dynamic conditions. The dynamic range and operating flexibility is expected to improve with the introduction of advanced alkaline electrolysers (Mathiesen et al., 2013). These electrolysers operate at higher temperature and pressure (up to 30 bars) but are currently at pre-commercial stage. Another advantage of pressurised electrolysis is that it yields high-pressure hydrogen which is needed in the case of subsequent synthesis of chemicals and fuels (Graves et al., 2011).

3.2.2 PEM electrolysis

The PEM electrolyser cell consists of a solid polymer that serves as electrolyte and membrane and it is operated at 50-80°C. The PEM electrolyser is less mature than the alkaline electrolyser; small PEM electrolyser units (up to 50 kW) have been commercially available for some time while units in the MW scale became available only recently (Götz et al., 2016). The practical experience of PEM electrolysis shows that the efficiency is usually higher than for alkaline electrolysis (Mathiesen et al., 2013).

The PEM electrolyser has so far been produced in small quantities since they are usually not cost competitive (Mathiesen et al., 2013). The PEM electrolyser suffers from high material costs caused by the use of a polymer membrane that contains noble metals (Götz et al., 2016). The life expectancy is currently less than 10 years (Mathiesen et al., 2013). The main advantages of the PEM electrolyser are its simple compact design, fast cold start and high flexibility. This electrolyser is thus well-suited for dynamic operation. PEM electrolysers (as well as alkaline electrolysers) are currently used in a number of ongoing power-to-gas demonstration projects (Gahleitner et al., 2013).

3.2.3 SOEC

The SOEC is an immature technology that is still at laboratory stage. The SOEC uses a solid ceramic electrolyte and electrodes of ceramic materials doped with rare earth metals. The electrolysis is carried out with steam at high temperatures (700-1000°C). The energy efficiency for a SOEC is expected to be around 77% (LHV) assuming the steam is generated by electric input (Mathiesen et al., 2013). The electricity-to-hydrogen efficiency could be up to about 90% assuming access to high-temperature heat (> 400°C) at the site (Mathiesen et al., 2013).

The SOEC is not commercially available, but recent developments and performance improvements have brought the technology close to the practical implementation (Graves et al., 2011). The long-term durability, however, still needs to be proven. The SOEC is expected to be the most competitive electrolyser technology in the future with regard to capital and operational costs (Graves et al., 2011). The technology is expected to become available at MW scale (Mathiesen et al., 2013.

The SOEC is preferably operated continuously due to the high temperature, but it can be operated dynamically if standby periods are avoided. Standby periods are undesirable since the cell temperature must be kept at the operating temperature in order to be able to respond fast and this leads to energy losses (Mathiesen et al., 2013). Unlike alkaline and PEM cells, the SOEC can be designed for dissociation of CO_2 or of CO_2 and steam (see Section 3.3.4).

3.2.4 Hydrogen storage

Hydrogen storage is often necessary if the electrolyser is intended to be dynamically operated since the electrolyser is usually more flexible than subsequent chemical synthesis. Intermediate storage for other gases, e.g. biogas and CO_2, may also be necessary but are less costly. The two best options for temporary hydrogen storage are high-pressure gas tanks (350-700 bars) or metallic hydrogen tanks (Götz et al., 2016). These are the storage methods used in current power-to-gas pilot plants around the world (Gahleitner, 2013). Another option is the storage of hydrogen in underground caverns. This could be the cheapest method but is mainly suited for high-capacity and long-term hydrogen storage (Götz et al., 2016).

3.3 Chemical and fuel production

3.3.1 CO_2 hydrogenation

The direct reaction between hydrogen and CO_2 is called hydrogenation. The end product of hydrogenation depends on the choice of catalyst and could be for example methanol or methane. In the case of methane, the hydrogenation is often referred to as methanation. The first step in hydrogenation is always the so-called reverse water-gas shift (RWGS) reaction, which is an endothermic reaction (R2), i.e. requires activation energy.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (R2)$$

3.3.2 Catalytic methanation

Methane production via CO_2 hydrogenation is usually called methanation which refers to the production of methane from CO_2 or CO and hydrogen. Catalytic or thermo-chemical CO_2 methanation is an equilibrium reaction, which is generally referred to as the Sabatier reaction (R3):

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (R3)$$

CO_2 methanation is an exothermic reaction that is carried out in two parallel processes; these include the RWGS reaction (R2) which is endothermic and CO methanation which is strongly exothermic. According to the mass and energy balance of the Sabatier reaction (R3), it is theoretically possible to produce 18.2 PJ of methane from 1 Mton of CO_2 and 22 PJ of hydrogen (see Appendix).

The Sabatier reaction is promoted by high pressure and low temperature. In reality the process is typically operated at a temperature of 200-550°C and elevated pressure (1-100 bars) (Götz et al, 2016). Several metals may be used as catalyst for the methanation reaction, but nickel is often considered to be the optimum choice of catalyst due to its relatively high activity, good methane selectivity and low raw material price (Götz et al, 2016). The nickel-based catalyst, however, requires high purity of the input gas and is very sensitive to impurities such as sulphur. In order to achieve high conversion efficiency, the temperature must be kept fairly constant and the H_2:CO_2 ratio should be around 4. The flexibility of the process is thus low.

The Sabatier reaction has been known for more than 100 years, but the development of the CO_2 methanation process largely relies on the research and experience of CO methanation. CO methanation gained importance for the production of synthetic natural gas (SNG) during the oil crises of the 1970s. CO methanation based on synthesis gas from coal gasification is state-of-the-art technology today and fixed bed methanation reactors have been commercially available for decades (Rösch et al., 2016). Catalytic CO_2 methanation for production of SNG has also been investigated for a number of decades (Götz et al., 2016). Basically the same reactors can be used in CO_2 methanation as in CO methanation, but there are also a handful companies that provide technologies that are tailor-made for CO_2 methanation using either CO_2 or biogas as feed (Rönsch et al., 2016). Catalytic CO_2 methanation has been tested in number of power-to-gas pilot or demonstration plants around the world, many of which are located in Europe (Bailera et al., 2017). One example is the Audi e-gas plant in Wertle, Germany, which opened in 2013. The plant is supplied with CO_2 that has been separated from raw biogas at a nearby biogas plant (Bailera et al., 2017).

The main advantage of catalytic methanation compared to biological methanation (see Section 3.3.3) is the faster reaction and thus smaller reactor volume required, which makes this technology more suitable in large-scale applications. The main disadvantage of this technology is currently the requirement of high purity input gas and low operational flexibility of the process. The operational flexibility is therefore the priority in current research activities (Rönsch et al., 2016).

3.3.3 Biological methanation

Biological methanation can be seen as part of the biogas production process where biological material is decomposed through several steps among which methanation is the final step. Biological methanation is the conversion of hydrogen and CO_2 to methane by methanogenic microorganisms of the cell type archea which serve as biocatalyst (Benjaminsson et al., 2013). The CO_2 and hydrogen must be dissolved in the broth (mainly water) in order to be available to the microorganisms which obtain their energy for growth from metabolising CO_2 and hydrogen. The overall process of biological methanation can be described by the Sabatier reaction in liquid phase where the CO_2 and hydrogen are dissolved in water (R4).

$$4H_2 + HCO_3^- + H^+ \rightleftharpoons CH_4 + 3H_2O \quad \text{(R4)}$$

There are two distinctly different process concepts: in situ biological methanation and biological methanation in a separate reactor.

In *in situ biological methanation* hydrogen is fed directly to the biogas digester. This approach is simple but makes it difficult to optimise the CO_2 methanation since the addition of hydrogen has a negative effect on the anaerobic process due to the pH increase (Luo et al. 2012). Another limitation is that it is difficult to achieve a total conversion of the CO_2 to methane (Götz et al., 2016).

Biological methanation in a separate reactor is not limited to the use of biogas as CO_2 source. Unlike in situ biological methanation, the process and reactor design can be adjusted to the requirements of the methanogenic microorganisms. Biological methanation takes place under anaerobic conditions at a temperature of 40-70°C and mostly ambient pressure (Götz et al., 2016). The process is generally carried out in a stirred tank reactor (Rönsch et al., 2016). It is possible to obtain a high concentration (almost 100%) of methane. However, the process is fairly slow and thus requires a large reactor volume in order to methanise a certain feed of biogas or CO_2. This volume is several orders of magnitude larger than for catalytic methanation in a fixed-bed reactor (Götz et al., 2016). The rate limiting step in biological methanation is the supply of hydrogen to the microorganisms. Hydrogen is much less soluble than CO_2 in water. Improving the hydrogen supply to the microorganisms is therefore a research priority for this technology (Götz et al., 2016). On the other hand, biological methanation has some important advantages compared to catalytic methanation. The advantages include high tolerance for impurities in the feed gas, higher operational flexibility and ambient pressure in the reactor (which eliminates the need for gas compression).

Biological methanation is a precommercial technology that is less mature than catalytic methanation. The technology is currently being investigated in a number of pilot and demonstration plants around Europe (Bailera et al., 2017). One example is one of MicrobEnergy's power-to-gas plants in Schwandorf that apply biological methanation in a separate reactor. This concept is also being demonstrated at Avedöre waste water treatment plant in Copenhagen within the project BioCat (Bailera et al., 2017).

3.3.4 Syngas production via co-electrolysis of CO_2 and steam

CO_2 can be used for production of syngas via co-electrolysis of CO_2 and steam. The process is rather complicated since it involves three main reactions that occur simultaneously: the electrolysis of CO_2 to CO, the electrolysis of water and the RWGS reaction (Mathiesen et al., 2013). By supplying the proper ratio of water (steam) and CO_2, the syngas can be produced with a composition tailored for the subsequent chemical synthesis. The reaction below (R5) illustrates co-electrolysis in combination with catalytic conversion of syngas with a H_2/CO ratio tailored for methane production.

$$CO_2 + 3H_2O \rightharpoonup 3\,H_2 + CO + O_2 \rightharpoonup CH_4 + H_2O + O_2 \qquad \text{(R5)}$$

Co-electrolysis of CO_2 and steam requires the deployment of a SOEC (see Section 3.2.3), which is still in the stage of research and development. The benefit of co-electrolysis is that it produces syngas which is used in the existing chemical synthesis of methanol via steam reforming natural gas and of SNG via coal/biomass gasification. The co-electrolysis of biogas or producer gas with steam is considered to be particularly promising (Quadrelli et al., 2015). In the case of biogas, it is important that the co-electrolysis is operated at process conditions that suppress steam reforming of methane since that would reduce overall efficiency (Haldor Topsoe, 2012).

3.3.5 Methanol synthesis from CO_2

Methanol is traditionally produced from syngas. Methanol can also be produced from CO_2, either in a one-step process (CO_2 hydrogenation) or in a two-step process (CO_2 hydrogenation via the RWGS reaction). In the two-step process part of the CO_2 is converted to CO through the RWGS reaction (R2). After removal of the water produced, the resulting gas is fed to a methanol synthesis reactor. Methanol synthesis via CO_2 hydrogenation is an exothermic equilibrium reaction, but initially requires heat. The overall reaction may be described with the following formula (R6):

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \text{(R6)}$$

According to the mass and energy balance of this reaction, it is theoretically possible to produce 14.3 PJ methanol from 1 Mton of CO_2 and 16.5 PJ of hydrogen (see Appendix). The formation of methanol is promoted by high pressure and low temperature. The one-step process is often carried out at a pressure of 50-100 bar, 200-300°C and over a catalyst containing copper and zinc oxide and sometimes various metal additives (Perez-Fortes et al., 2015). Methanol synthesis via CO_2 hydrogenation entails lower heat losses than CO_2 methanation since the reaction requires less hydrogen in relation to end product. However, the process is more complicated since it is thermodynamically unfavourable. In order to achieve a high yield, the unreacted CO_2 must be recirculated and the process operated at high pressure (Mohseni, 2012).

The production of methanol from CO_2 is currently at pilot and demonstration scale with a number of plants around the world (Armstrong, 2015). In 2011, Carbon Recycling International started the operation of the first commercial demonstration plant in Iceland. The plant uses the one-step process and has a capacity to produce 5 Mt of methanol per year. The CO_2 is derived from geothermal steam that is used in a nearby power plant (Perez-Fortes et al., 2015). Wider deployment of methanol production from CO_2 is considered to be limited by economics rather than technological readiness (Dowson and Styring, 2015).

3.3.6 Hydrocarbon production via Fischer-Tropsch synthesis

The Fischer-Tropsch process can produce a variety of hydrocarbons from synthesis gas depending on the process and reaction conditions such as the choice of catalyst, syngas ratio and reactor temperature and pressure (France et al., 2015). The Fischer-Tropsch process yields a broad range of hydrocarbons, but the process can be optimised towards certain ranges of products. The process can be operated according to two distinctly different temperature regimes. The high-temperature (300-350°C) process in combination with an iron-based catalysts yields low-molecular mass olefins. The low-temperature (200-240°C) process in combination with an iron or cobalt-based catalyst yields diesel and high-molecular mass linear waxes (Graves et al., 2011).

The Fischer-Tropsch process is exothermic and can be described by the following reaction (R7):

$$2H_2 + CO \rightleftharpoons -CH_2- + H_2O \qquad \text{(R7)}$$

The Fischer-Tropsch processes is a relatively mature technology that has been applied in a number of countries for periods of time for production of synthetic hydrocarbon fuels such as petrol and diesel (France et al., 2015). It should be noted that the production of long hydrocarbon chains such as those in petrol and diesel requires many process steps, which in turn leads to energy losses being higher than for production of methane and methanol (Mohseni, 2012).

3.3.7 Polymer production

Polymers are the main component of plastics, which usually also contain different additives. Polymers can be produced from various feedstocks, among which olefins are the most common. Ethylene and propylene are the most widely used olefins and the major feedstocks in the production of polymers such as polyethylene, polypropylene, polyethylene terephtalate (PET), polyvinylchloride (PVC).

CO_2 can be transformed into polymers via two routes. The direct route involves the utilisation of CO_2 as a polymer building block and the indirect route involves the production of polymer building blocks from CO_2 or CO_2 derived chemicals (Langanke et al., 2015). The most prominent example of the direct route is the catalytic co-polymerisation of epoxides with CO_2 towards polyether carbonates (Langanke et al., 2015).

The indirect route offers larger potential for CO_2 utilisation than the direct route and includes polymer production from CO_2-derived compounds, such as methane, methanol and urea (urea is not discussed in this report). Both methane and methanol can be converted into light olefins.

Methanol can be catalytically converted into various light olefins via the so-called methanol-to-olefin (MTO) pathway. In this process methanol is first dehydrated into dimethyl ether (DME). The resulting mixture of DME and water is then converted to light olefins (C2-C4) (France et al., 2015). This process is currently applied at commercial scale in China (Alvarado, 2016a).

Methane can be converted to ethylene via oxidative coupling. This process is commercially unproven and suffers from low yield. By 2050 the conversion rate is expected to be around 35% and the selectivity for ethylene at 35% (Palm et al., 2016).

4 Options for integrated CO_2 utilisation in biomass conversion processes

This chapter describes different options for integrated CO_2 utilisation in different biomass conversion processes for production of methane and methanol. A number of these options are illustrated below with simplified flow charts; these charts exclude e.g. units for compression and chemical purification (water removal via condensation or distillation). Hydrogen storage is also not included, but may be required if the electrolyser is to be operated dynamically. In order to facilitate comparison between the different options, the illustrated examples are based on an annual biomass input of 10 PJ for combustion, fermentation and thermal gasification and of 100 TJ for anaerobic digestion. The chemical synthesis of methanol and methane is calculated based on the mass and energy balances that are shown in the appendix. These stoichiometric balances represent the maximum theoretical conversion feasible. A 5% conversion loss is therefore assumed for the chemical synthesis, which is in line with the assumptions by Connelly et al. (2014).

4.1 Biomass combustion

As described in Section 3.1.2 there are different options for CO_2 capture from combustion systems. The feasibility and costs of these options are highly dependent on site-specific circumstances, including the size, age and type of unit. Sections 4.1.1-4.1.2 below illustrate post CO_2 capture and oxyfuel combustion. Pre-combustion, which involves gasification, is addressed in Section 4.4.

4.1.1 Post CO_2 capture

In the case of retrofitting of an existing biomass-fired CHP plant or a waste incineration plant that utilise boiler technology and steam turbine, post combustion CO_2 capture is probably the most suitable option. This can be accomplished by integrating an amine scrubber to the existing plant. Figure 5 illustrates a biomass-fired CHP plant that uses an amine scrubber for CO_2 capture and produces methanol via CO_2 hydrogenation and synthesis. The overall efficiency of the CHP plant is assumed to be 90 % (based on LHV) and the CO_2 generation to be 100 kg of CO_2 per GJ of solid biomass. Furthermore, it is assumed that 90% of the CO_2 in the flue gases is captured and that the energy demand for the capture of 1 tonne of CO_2 is 3.0 GJ of heat and 0.9 GJ of electricity (based on average values from IPCC (2005)).

The electrolyser capacity required for producing a certain amount of hydrogen depends on how it is operated. If the CHP plant and electrolyser operate 8000 full load hours per year (this is a high capacity factor for a CHP plant that delivers district heat), the installed capacity of the electrolyser must be 736 MW.

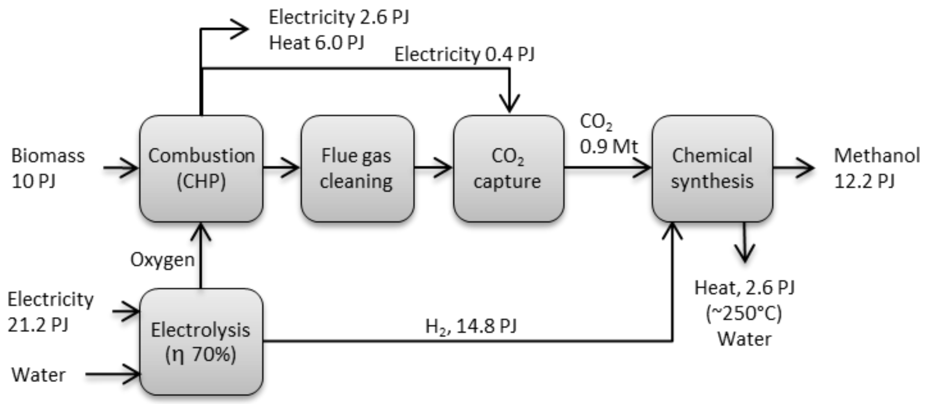

Figure 5: Biomass combustion with post combustion CO_2 capture followed by methanol synthesis. The CO_2 capture is assumed to require 3.0 GJ of heat and 0.9 GJ of electricity per tonne of CO_2 captured (IPCC, 2005). The methanol synthesis is based on the mass and energy balance (see appendix) and 5% conversion losses.

4.1.2 Oxyfuel combustion

Oxyfuel combustion is an attractive option if designing a new biomass-fired CHP plant with CO_2 capture and utilisation since the oxygen can be provided at low cost from the electrolyser. In oxyfuel combustion, the biomass is combusted in a mixture of oxygen and recirculated flue gases. This leads to a high concentration of CO_2 in the flue gases and thus simplified CO_2 separation. Figure 6 illustrates a CHP plant that applies oxyfuel combustion and where the captured CO_2 is used for methanol production. All of the oxygen required for the combustion can be supplied by the electrolyser. The CO_2 capture processes is assumed to require 0.45 GJ of electricity per tonne of CO_2, ie. half of the electricity required in post CO_2 capture, but no heat; this is a rough assumption based on Darde et al. (2009).

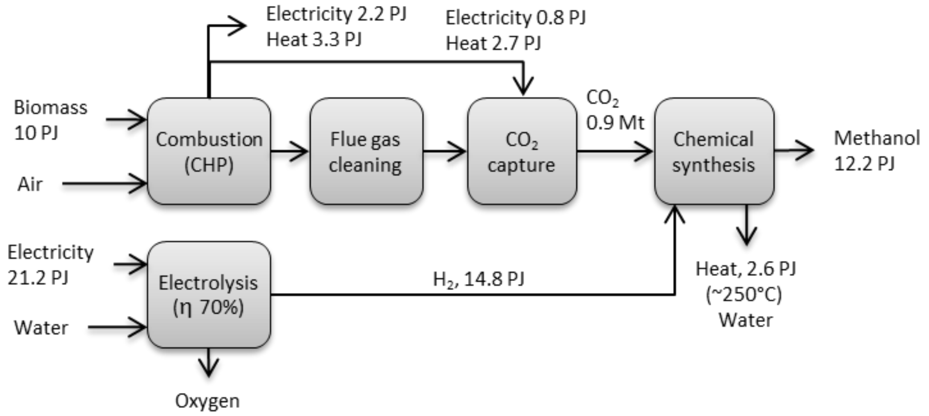

Figure 6: Oxyfuel combustion of biomass followed by hydrogenation and methanol synthesis. The process involves recirculation of the flue gases. The CO_2 capture is assumed to require 0.45 GJ of electricity per tonne of CO_2 captured. The methanol synthesis is based on the mass and energy balance (see appendix) and 5% conversion losses.

4.2 Anaerobic digestion

Biogas from anaerobic digestion contains 30-50% CO_2 that could be used for production of methane or other chemicals. Methane is a particularly attractive product since it is the major component in biogas (typically 50-70%) and since hydrogenation of biogas could replace traditional upgrading technologies (typically water scrubbing or PSA). There are three main technical options for upgrading with hydrogen: i) catalytic methanation, ii) biological methanation and iii) co-electrolysis followed by CO methanation.

4.2.1 Biogas upgrading using catalytic methanation

Biogas upgrading using catalytic methanation can be designed in different ways. For biogas plants that have traditional upgrading equipment installed it is possible to apply catalytic methanation on the separated CO_2. At a plant that lacks this equipment it is more attractive to feed the biogas to the methanation reactor, thus making investments in other upgrading technology unnecessary (Benjaminson et al., 2013). This latter concept is illustrated in Figure 7. Before the biogas enters the reactor it must undergo desulphurisation since biogas contains high amounts of sulphur compounds (up to 1%) which the nickel-based catalysts in the reactor are very sensitive to. Catalytic methanation is an exothermic and high-temperature reaction that generates steam. The process enables the production of high concentration methane. In the illustrated example in Figure 7, the methane yield is almost doubled, assuming the biogas contains 50% CO_2. The system in Figure 7 requires an installed electrolyser capacity of at least 4.2 MW if the unit is operated 8000 full load hours per year and of at least 11 MW if it is operated 2000 full load hours per year.

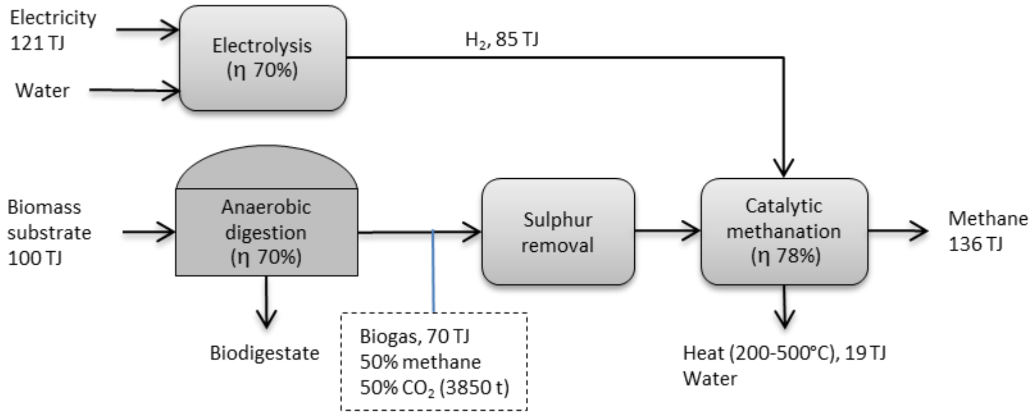

Figure 7: Anaerobic digestion and biogas upgrading via catalytic methanation. The figure was produced with data on anaerobic digestion from Benjaminson et al. (2013) and based on the mass and energy balance for methanation (see appendix) including an assumption of 5% losses in the methanation.

4.2.2 Biogas upgrading using biological methanation

As described in Section 3.3.3 there are two concepts for biological methanation: in situ biogas upgrading and biological upgrading in a separate reactor. In situ biogas upgrading offers an opportunity to increase the methane content of the biogas without investing in a separate reactor. The results from a pilot project in Schwandorf, Germany, suggest that in situ biogas upgrading can increase the methane content from 50 to 75% (Benjaminson et al., 2013). In situ biogas upgrading, however, requires the use of additional upgrading technology in order to produce 100% methane.

Biogas upgrading using biological methanation in a separate reactor enables a higher methane concentration than in situ biogas upgrading. In theory, the methane concentration could be as high as in catalytic methanation, i.e. almost 100%, which is illustrated in Figure 8. The concentrations achieved so far in pilot plants are, however, often lower (Götz et al., 2016). Biological methanation is carried out at relatively low temperature and generates waste heat of around 60°C. This heat can be used for heating the anaerobic digester.

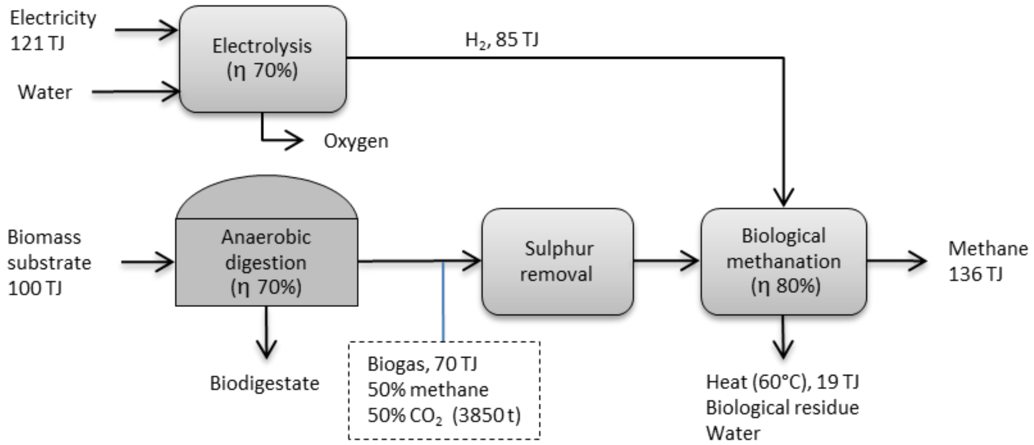

Figure 8: Anaerobic digestion and biogas upgrading via biological methanation in a separate reactor. The figure was produced with data on anaerobic digestion from Benjaminson et al. (2013) and based on the mass and energy balance for methanation (see appendix) including an assumption of 5% losses in the methanation.

4.2.3 Biogas upgrading using co-electrolysis

Biogas can also be upgraded via co-electrolysis of biogas with steam in a SOEC. The gas mixture from the SOEC consists of methane and syngas, which then undergo CO methanation. The heat generated from the catalytic methanation can be used in the SOEC. This process route is illustrated in Figure 9.

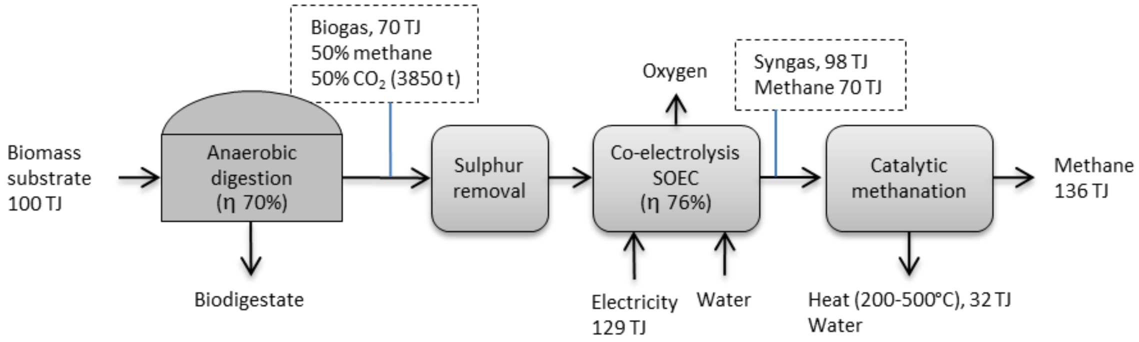

Figure 9: Biogas upgrading using co-electrolysis of biogas and steam followed by catalytic methanation for production of methane. The figure was produced with data on anaerobic digestion from Benjaminson et al. (2013) and based on the mass and energy balance for co-electrolysis and methanation (see appendix) including an assumption of 5% losses in the methanation.

4.3 Fermentation

The fermentation at ethanol production plants releases a gaseous stream containing about 99% CO_2. The only separation required is dehydration (removal of water vapour) (Xu et al., 2010). One option is to utilise this CO_2 to produce methanol via hydrogenation and methanol synthesis, which is illustrated in Figure 10. This concept increases the total alcohol production by almost 50%. The ethanol plant in Figure 10 uses dried cereals as input and is supplied by heat from a nearby CHP plant fired with straw. A further development of this ethanol plant would be to also utilise the straw for ethanol production via combined hydrolysis and fermentation. This produces a co-product lignin that could be used as fuel in the CHP plant. Combined hydrolysis and fermentation also enables the use of wood chips as raw material in ethanol production.

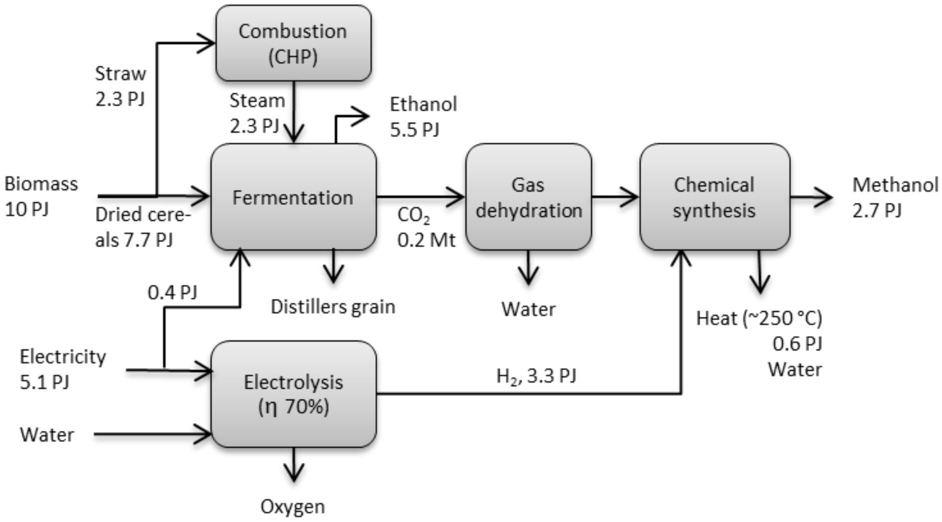

Figure 10: Ethanol production via fermentation and CO_2 utilisation via hydrogenation and methanol synthesis. The figure was produced with data on ethanol production from Martin et al. (2010) and on the mass and energy balance for methanol synthesis, including an assumption of 5% losses in the methanol synthesis.

4.4 Biomass gasification for production of chemicals

Biomass gasification with subsequent chemical synthesis releases CO_2 since the producer gas contains too much carbon in relation to hydrogen for most chemical products. The excess CO_2 can be utilised via hydrogenation of the producer gas or via co-electrolysis of the producer gas and steam. It is also possible to separate the CO_2 from the producer gas after the producer gas has been conditioned in a water gas shift reactor, and then to utilise this CO_2 separately. This latter configuration corresponds to the pre-combustion system described in Section 3.1.2. Unlike anaerobic digestion and fermentation that produce biogas and ethanol, respectively, gasification technology can be employed as a first step for production of various chemicals and fuels, including e.g. methane, methanol, DME and FT-hydrocarbons.

Hydrogenation of the producer gas is especially attractive in combination with oxygen-blown gasification since the gasifier can be fed oxygen from the electrolyser. Figure 8 shows two flow charts of oxygen-blown biomass gasification and synthesis of biomethane/renewable methane, one with a traditional set up that releases CO_2 and one which integrates CO_2 hydrogenation. By integrating CO_2 hydrogenation in the process, the yield of methane can be doubled. The concept that includes hydrogenation of the producer gas requires investment in an electrolyser, but at the same time does not need a final CO_2 removal unit and a water-gas shift reactor, which adjusts the CO/H_2 ratio.

Hydrogenation of the producer gas is also possible in combination with steam gasification, which is illustrated in Figure 12. In this case, the hydrogenation of the producer gas increases the methanol yield by 45%. The gasification reactor is supplied by steam from a nearby CHP plant.

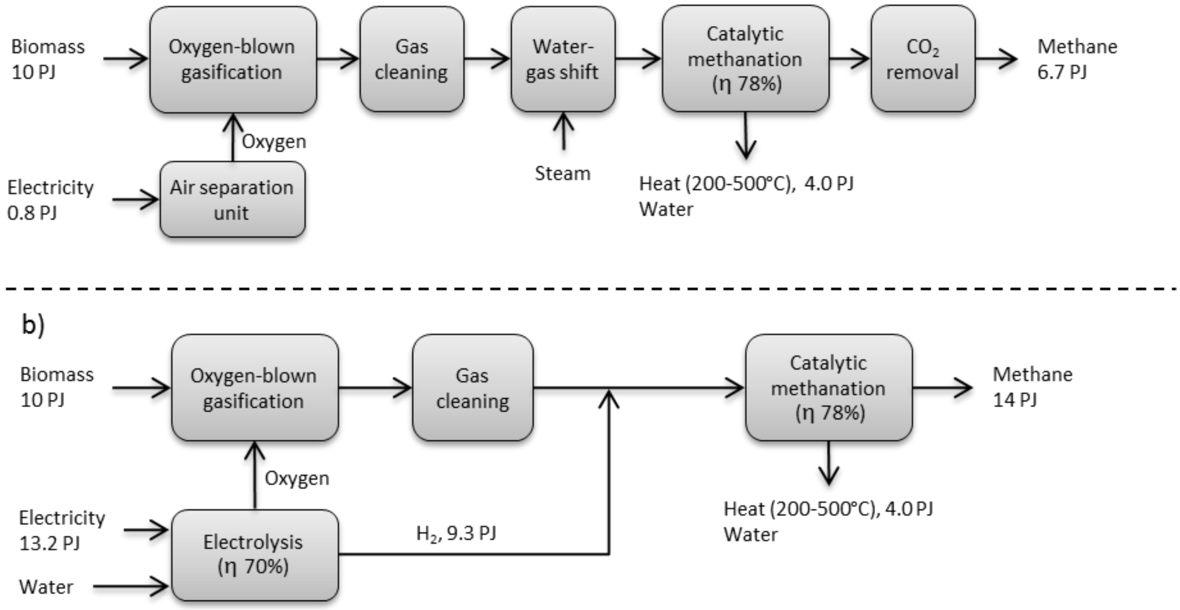

Figure 11: Both figures illustrate thermal gasification using an oxygen-blown gasifier followed by catalytic methanation. a) shows the traditional concept which releases biogenic CO_2 and b) shows a concept where the producer gas is hydrogenated before methanation. The figures have been designed with data from Götz et al. (2016) and Mozaffarian et al. (2003).

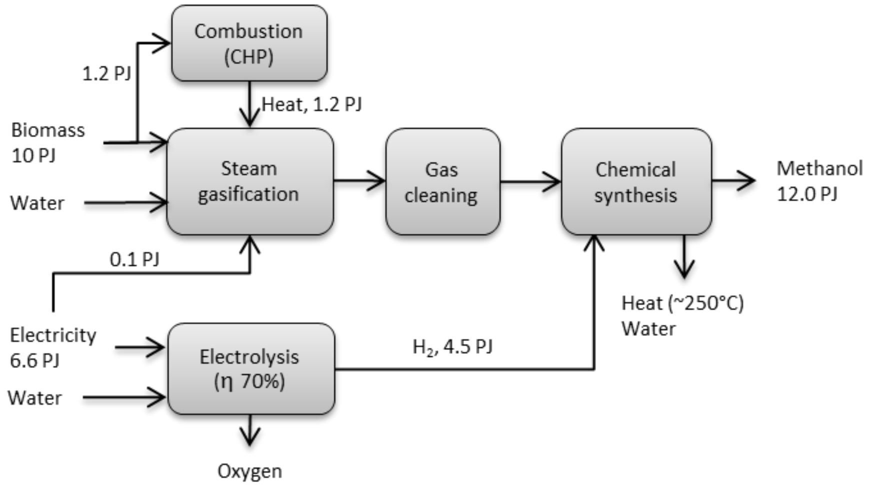

Figure 12: Steam gasification, CO_2 hydrogenation and methanol synthesis. The figure is based on data from Connelly et al. (2014) concerning steam gasification and on the mass and energy balance for methanol synthesis, including an assumption of 5% losses.

5 Techno-economic assessment of different process routes

This chapter contains a techno-economic assessment of different process routes for the production of chemicals and fuels from electricity and biogenic CO_2. It presents: estimates of the generation of biogenic CO_2 based on the current and possible future use of biomass; the energy input-output balances of different process routes; the main cost drivers and the production cost of CO_2-based methanol; the potential production of chemicals and the electricity requirements for this; and a SWOT analysis of the opportunity to utilise CO_2 from different biomass conversion processes.

5.1 Total generation of biogenic CO_2

The total annual generation of CO_2 from biomass conversion processes (that are relevant for CO_2 utilisation) and waste incineration in Europe is estimated to 395 Mt CO_2 (Table 3). Most of this CO_2 originates from biomass combustion (287 Mt) and waste incineration (81 Mt). The CO_2 generation in biogas production is estimated to 23 Mt. The CO_2 generated from ethanol production is estimated to 4.4 million tonne, about 10% of which is currently used.

Table 3: The estimated generation of CO_2 from different biomass conversion processes (that are relevant for CO_2 utilisation) and waste incineration in Europe. The estimates are based on data for OECD Europe in 2014 (IEA, 2016; ePURE, 2015).

Biomass conversion process	**Biomass use (PJ/y)**	**Biogenic CO_2 (Mt/y)**	**Main conversion product**
Combustion of biomass and municipal renewable waste			In total: 168 TWh electricity, 139 TWh DH, unknown amount of process heat
- central transformation	2030	203[a]	
- industry	840	84[a]	
Waste incineration			In total: 23.5 TWh el., 116 PJ DH
- municipal non-renewable waste	400	57[b]	
- industrial waste	170	24[b]	
Anaerobic digestion	900[c]	23[d]	633 PJ biogas
Fermentation	220[e]	4.4[f]	121 PJ ethanol (5.8 million m^3)
Total	4560	395	

[a] Based on an approximated CO_2 emission factor of 100 kg/TJ.

[b] See CO_2 emission factor in Table 1.

[c] Calculated based on the assumption that 70% of the biomass substrate is converted to biogas.

[d] Calculated based on the assumption that the biogas contains 40% CO_2.

[e] Calculated based on the assumption that 55% of the biomass input (starch based crop including the straw) is converted to ethanol and that the straw is used in a CHP plant that supplies heat to the fermentation process (Martin et al., 2010).

[f] Calculated based on the assumption that the production of 1 m^3 ethanol yields 0.76 t CO_2.

The use of biomass in OECD Europe has more than doubled since 1990 (see Figure 1) and could continue to increase in the future. Various biomass assessments indicate that it is possible to increase the supply of biomass in Europe. For example, the potential supply of biomass in the EU25 has been estimated to up to 18 EJ/yr by Ericsson and Nilsson (2006) and to 12.4 EJ/yr by EEA (2006).

An increased use of biomass in the future would increase the generation of biogenic CO_2. To what extent this would entail more biogenic CO_2 that is suitable for utilisation depends on how the biomass use is allocated between different conversion processes. Table 1 presents the estimated generation of biogenic CO_2 for two different allocation scenarios that both assume an annual biomass use of 12 EJ. This biomass use is about double to that in 2014 which amounted to 5.6 PJ. Both scenarios assume that 3 EJ of biomass is used in anaerobic digestion. The remaining 9 EJ is used in either centralised combustion or oxygen-blown gasification. The generation of biogenic CO_2 amounts to about 980 Mt/y in the combustion scenario and to about 460 Mt/yr in the gasification scenario.

Table 4: The estimated generation of biogenic CO_2 for two allocation scenarios that assume a total biomass use of 12 EJ/yr.

Allocation scenario	**Biomass conversion process**	**Biomass use (EJ/y)**	**Biogenic CO_2 (Mt/y)**
Combustion	Combustion Anaerobic digestion	9.0 3.0	900 77
	Total	12.0	977
Gasification	Oxygen blown gasification Anaerobic digestion	9.0 3.0	380 77
	Total	12.0	457

5.2 Energy input-output balances

Table 5 presents an overview of the energy input-output balances for the process routes that are illustrated in Section 4 and is based on the efficiencies used there. The electricity-to-fuel (hydrogen or syngas) efficiencies of the electrolyser are assumed to be 70% for electrolysis of water and 76% for co-electrolysis of CO_2 and steam. The assumed efficiencies thus reflect good performing low-temperature electrolysis or high-temperature electrolysis with no access to high-temperature waste heat, i.e. the heat is generated by electricity.

The total efficiencies of the studied biomass and CO_2 conversion processes are estimated to be 54-72% and to be highest for steam gasification with chemical synthesis (in this case of methanol). The CCU efficiencies, i.e. the output of CO_2-derived chemicals in relation to the dedicated energy input for CCU, were estimated to a range of 49-57%. The CCU efficiency is the lowest for post CO_2 capture and chemical synthesis due to the high energy requirements for CO_2 capture.

Table 5: An overview of biomass and electricity inputs, the chemical outputs (CO_2-derived output in parentheses) and estimated efficiencies for different process routes. The table is based on the data presented in Section 4, most importantly 70% efficiency (electricity-to-hydrogen) for water electrolysis and 76% for co-electrolysis.

Biomass and CO_2 conversion process	**Input (PJ)**			**Output (PJ)**			**Total efficiency[h]**	**CCU efficiency[a]**
	Bio-mass	**Electricity**		**MeOH**	**Methane**	**Other**		
		Electro-lysis	**Other**					
Combustion and post CO_2 capture and synthesis	10	21.2	0.8	12.2 (12.2)	-	3.0 (el)[b] 6.0 (heat)[c]	57% [e]	49%
Oxyfuel combustion and synthesis	10	21.2	0.4	12.2 (12.2)	-	3.0 (el)[d] 6.0 (heat)	67% [e]	56%
Anaerobic digestion and methanation	10	12.1	-	-	13.6 (6.6)	-	62%	55%
Anaerobic digestion, co-electrolysis and methanation	10	12.9	-	-	13.6 (6.6)	-	59%	51%
Fermentation and methanol synthesis	10[f]	4.7	0.4	2.7 (2.7)	-	5.5 (EtOH)	54%	57%
Oxygen blown thermal gasification and methanation	10	13.2		-	14 (7.3)	-	60%	55%
Steam gasification and methanol synthesis	10[g]	6.5	0.1	12.0 (3.7)	-	-	72%	57%

[a] Output of CO_2-derived methanol or methane in relation to electricity input.

[b] All electricity produced, including the electricity (0.8 PJ) that is used for CO_2 capture.

[c] All heat produced, including the heat (2.7 PJ) that is used for CO_2 capture.

[d] All electricity produced, including the electricity (0.4 PJ) that is used for CO_2 capture.

[e] Calculated based on net output/net input.

[f] 2.3 PJ of this biomass is used for generation of steam.

[g] 1.2 PJ of this biomass is used for generation of steam.

[h] Total output of methanol, methane, electricity and heat in relation to the input of electricity and biomass.

Ongoing research efforts into the SOEC suggest that this technology will be available in the future and could offer very high electricity-to-hydrogen efficiencies, given that there is access to high-temperature heat (>400°C) that can provide heat to the high-temperature electrolysis process (Graves al., 2011). The operational flexibility is, however, likely to be lower for the SOEC than low-temperature electrolysis (Mathiesen et al., 2013). Chemical synthesis that involves exothermic reactions can provide medium (> 150°C) or high-temperature heat. Catalytic methanation and methanol synthesis could provide heat of 200-500°C to the SOEC, but additional heating would be necessary in order to meet the temperature requirement (>700°C). Assuming the SOEC can be heated by internal sources of "waste heat" via heat integration could motivate the use of 90% as electric efficiency of the electrolyser in the calculations.

Table 6 presents the energy inputs and outputs for the process routes in Table 5, but based on an electric efficiency of 90 % for the electrolyser. The total efficiencies of the studied biomass and CO_2 conversion processes are estimated to be 58-79% and to be highest for steam gasification with chemical synthesis (in this case of methanol). The CCU efficiencies, i.e. the output CO_2-derived chemical in relation to the energy input, are estimated to a range of 61-74%.

Table 6: An overview of the biomass and electricity inputs, the chemical outputs (CO_2-derived output in parentheses) and the estimated efficiencies for different process routes. The table is based on electrolyser electric efficiency of 90%.

Biomass and CO_2 conversion process	**Input (PJ)**			**Output (PJ)**			**Total efficiency**[h]	**CCU efficiency**[a]
	Bio-mass	**Electricity**		**MeOH**	**Methane**	**Other**		
		Electro-lysis	**Other**					
Combustion and post CO_2 capture and synthesis	10	16.5	0.8	12.2 (12.2)	-	3.0 (el)[b] 6.0 (heat)[c]	67%	61%
Oxyfuel combustion and synthesis	10	16.5	0.4	12.2 (12.2)	-	3.0 (el)[d] 6.0 (heat)	78% [f]	72%
Anaerobic digestion and methanation	10	9.4	-	-	13.6 (6.6)	-	70%	70%
Anaerobic digestion, co-electrolysis and methanation	10	10.9	-	-	13.6 (6.6)	-	65%	61%
Fermentation and methanol synthesis	10[f]	3.7	0.4	2.7 (2.7)		5.5 (EtOH)	58%	73%
Oxygen blown thermal gasification and methanation	10	10.3	-	-	14 (7.3)	-	69%	71%
Steam gasification and methanol synthesis	10[g]	5.0	0.1	12.0 (3.7)	-	-	79%	74%

[a] Output of CO_2-derived methanol or methane in relation to energy input.

[b] All electricity produced, including the electricity (0.8 PJ) that is used for CO_2 capture.

[c] All heat produced, including the heat (2.7 PJ) that is used for CO_2 capture.

[d] All electricity produced, including the electricity (0.4 PJ) that is used for CO_2 capture.

[e] Calculated based on net output/net input.

[f] 2.3 PJ of this biomass is used for generation of steam.

[g] 1.2 PJ of this biomass is used for generation of steam.

[h] Total output of methanol, methane, electricity and heat in relation to the input of electricity and biomass.

Heat integration between different process units is essential in order to achieve high total energy efficiencies for the studied process routes. Catalytic methanation and methanol synthesis generate medium (150-400°C) or high-temperature heat (>400°C) while low-temperature electrolysis and biological methanation generate heat of low temperature (<150 °C). A number of processes require medium- or high-temperature heat and then leave behind waste heat of somewhat lower temperature; some examples are high-temperature electrolysis, post CO_2 capture, chemical purification (distillation), steam gasification and fermentation. Anaerobic digestion on the other hand requires heat of low temperature. Heat integration could also extend to external facilities and take the form of industrial symbiosis and/or involve deliveries of low-temperature waste heat to local district heating networks.

The energy balances in Table 5 and Table 6 include important energy flows and thus exclude the mass flows of water and oxygen. Water electrolysis requires large amounts of water. At the same time, methanol synthesis and catalytic methanation produce large amounts of water which in theory could provide half of the water required for electrolysis (see the mass and energy balances in the Appendix). Water electrolysis also produces enough oxygen to accommodate the need for oxygen in the process routes that involve oxyfuel combustion and oxygen-blown gasification.

5.3 Economics

This section focuses on identifying and assessing the main cost drivers related to the utilisation of CO_2 from different biomass conversion processes. This section does not provide a comprehensive cost assessment, but rather focuses on the capital and operational costs of the main processes, i.e. electrolysis, carbon capture and chemical synthesis (and purification). Table 7 summarises some important data on costs and Box 2 presents cost calculations for the main process steps of CO_2-based methanol production at a biomass combustion plant.

Table 7: Cost data of important processes related to CO_2 utilisation.

	Electrolyser[a]	**Catalytic methaniser**[b]	**Post CO_2 capture**[c]	**Oxyfuel combustion**[c]	**Unit**
CAPEX	0.9	0.05	0.9	1.0	M €/MWinput
Fixed O & M	4	10	2.5	3	% of capex/yr
Variable O&M	~cost of electricity	-	1.6	0.32	€/MWh input

[a] Mathiesen et al., 2013
[b] Vandewalle et al., 2015
[c] Energistyrelsen, 2012

Most studies show that the **cost of electrolysis** is the most important cost driver for CO_2 utilisation (see e.g. Graves et al., 2011; Götz et al., 2016; Vanderwalle et al., 2015). This is also supported by the calculations in Box 2. The cost of electrolysis is generally high and encompasses an important trade-off between the capital and operational cost (more on this in the next paragraph). The capital cost is determined by a number of factors, including capital expenditure (investment), lifetime, interest rate and operational hours (which determine the required installed capacity). The economy of scale is limited for electrolysis compared to other technologies. Alkaline electrolysis requires an investment of around 0.8-0.9 M€/MW[10] and is currently the most competitive technology. The SOEC is expected to become the cheapest technology in the future when it reaches maturity (see Table 2).

The variable operational cost of an electrolyser is dominated by the cost of electricity; the cost of water is negligible in comparison (Vandewalle et al., 2015). The cost of electricity is the most important cost driver if the electrolyser is operated continuously or with high full load hours (Götz et al., 2016). If the electrolyser is operated only during hours of very low electricity prices, the capital cost could be equally important. Furthermore, dynamic operation of the electrolyser is likely to require investment in hydrogen storage since downstream chemical synthesis is often less flexible. The capital expenditure for hydrogen storage is usually the second-largest investment at a power-to-gas plant (Götz et al., 2016).

The **cost of CO_2 capture** varies considerably between different biomass conversion processes. The cost is high for biomass combustion and could be zero in the case of utilisation of CO_2 from anaerobic digestion and thermal gasification where CO_2 separation is not necessary. Future costs of CO_2 capture from combustion systems are highly uncertain due to the lack of installations of this technology at commercial scale. The costs are likely to be highly dependent on site-specific circumstances, including the size, age and type of unit. The total cost of CO_2 capture for combustion installations has been estimated to be at best 25-50 €/t CO_2 (Energistyrelsen, 2012). This cost range is probably only valid for very large installations that are operated with high load factor since the capture technologies are associated with scale economy. The calculations presented in Box 2 indicate that the cost of CO_2 capture is considerably smaller than the cost of electrolysis; in this particular example the cost of CO_2 capture is estimated to 42 €/t CO_2.

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[10] 0.9 M €/MW (for 2020-2030) according to Mathiesen et al. (2013) and around 0.8 M €/MW according to Götz et al (2016) and Vandewalle et al (2015).

The **costs of chemical synthesis and purification** are considerably smaller than the cost of electrolysis and CO_2 capture from biomass combustion (see Box 2). The capital expenditure for a catalytic methaniser has been estimated to about 0.05 M€/MW (Vandewalle et al., 2015). The capital expenditure for CO_2 based methanol synthesis (via CCU) and purification has been estimated to about 0.09 M€/MW[11]; about 85% of this expenditure concerns the compression systems and the heat exchanger network while the capital expenditure for reactor and distillation column is comparatively small (Pérez-Fortes et al., 2015). Economy of scale is likely to be an important factor in methanol synthesis (Goeppert et al., 2014). The cost of the CO_2-derived chemical synthesis varies between process routes and depending on if there are synergies with the main product of the biomass conversion process. CO_2 utilisation related to biomass gasification and anaerobic digestion is advantageous in this regard. In the case of thermal gasification with chemical synthesis, the integration of CO_2 utilisation increases the capacity required in the chemical synthesis and purification processes, but no new processes are required. In the case of anaerobic digestion, the integration of CO_2 utilisation requires an investment in a methaniser reactor (except for in situ biogas upgrading), but eliminates the need for other biogas upgrading technology.

Water electrolysis produces a large amount of oxygen that is usually considered a by-product and not valorised in economic assessments. There are a number of options for **oxygen valorisation**. Two options that are addressed in this report are oxyfuel combustion and oxygen-blown gasification. The access to cheap oxygen from the electrolyser makes these technologies more attractive than if the oxygen would have to be produced via air separation.

The **production cost** of methanol from electricity and biogenic CO_2 in flue gases is estimated to about €780/t methanol (i.e. €120/MWh), when adding the costs for the basic process steps and assuming an electricity price of €50/MWh (see Box 2). This may be an underestimation of the total production cost since only the costs for the basic process steps are included. In this example, the cost of electricity and the overall cost of electrolysis accounted for 70% and 89%, respectively, of the total production cost. Connelly et al. (2014) have estimated the future (2050) production cost of methanol from CO_2 from flue gases to about €570/t. Their estimate is based on slightly different assumptions, e.g. an electricity cost of €43/MWh.

The market price of methanol varied in the range of €240-500/t methanol in the period 2010-2016 (Alvarado, 2016). The production of methanol from CO_2 and electricity can under most circumstances not meet the current market price of methanol which is set by the production based on natural gas or other fossil feedstocks (see Box 1). An exception to this would be CO_2-based methanol production located at a place with very low electricity prices. The competitiveness of CO_2-based methanol and methane is thus largely dependent on the cost relation between electricity and fossil feedstocks.

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[11] This value was calculated based on a CCU methanol plant that is presented in Pérez-Fortes et al. (2015). The plant produces 440,000 t of methanol and required an investment of 27 M€.

Box 2: Cost calculations for the basic process steps of CO_2-based methanol production at a biomass combustion plant (10 PJ biomass) with post CO_2 capture (see Figure 5)

Overall assumptions: lifetime of 20 years (n=20), interest rate of 5% (r= 0.05), 8000 full load hours; the production of 12.2 PJ of methanol (= 537,000 t). The annual capital cost is calculated with the formula below:

$$\text{Annual capital cost} = \text{capital expenditure} \times \frac{r}{1-(1+r)^{-n}}$$

Electrolysis:

Assumptions: hydrogen production of 14.8 PJ/yr, electricity consumption of 5.9 TWh/yr, capital expenditure of 0.9 M€/MW_e, fixed O & M of 4% of capex/yr, electricity cost of €50/MWh

The required capacity of the electrolyser is calculated to 737 MW, which leads to a capital expenditure of 663 M€.

=> capital cost = 53 M€/yr
=> fixed O & M cost = 26.5 M€/yr
=> variable cost = 295 M€/yr

=> total cost = 374 M€/yr or €696/t methanol

Post CO_2 capture:

Assumptions: biomass input of 10 PJ, capital expenditure of 0.9 M€/MW_{input}, fixed O & M of 3 % of capex/yr, variable O & M of €1.6/MWh_{input}, CO_2 separation of 0.9 Mt/yr

The required capacity of the biomass plant is calculated to 347 MW, which leads to a capital expenditure of 312 M€.

=> capital cost = 25
=> fixed O & M cost = 9 M€/yr
=> variable O & M cost = 4 M€/yr

=> total cost = 38 M€/yr or (€42/t CO_2) or €71/t methanol

Methanol synthesis and purification

Assumptions: capital expenditure (reactors, compressors, heat exchangers and distillation column) of 0.09 M€/$MW_{methanol}$ (Pérez-Fortes et al., 2015); fixed O & M of 10% of capex/yr.

The required capacity of the reactor is calculated to 424 MW, which leads to a capital expenditure of 38 M€.

=> capital cost = 3.0 M€/yr
=> fixed O & M cost = 3.8 €/yr

=> total cost = 6.8 M€/yr or €13/t methanol

In total (electrolysis + post CO_2 capture + methanol synthesis and purification)

Total cost = 419 M€/yr or €780/t methanol

5.4 Potential production of chemicals and the electricity requirements

The total generation of CO_2 from biomass conversion processes (that are relevant for CO_2 utilisation) and waste incineration in Europe was estimated to 395 Mton CO_2 (see Section 2.3) based on the biomass use in 2014. This is twice the amount of CO_2 that is needed to cover the annual need for carbon in the production of plastics in Europe, which has been estimated to 180-190 Mt/yr by Palm et al. (2016). Table 8 illustrates how much methane and methanol that can be produced from 395 Mt of CO_2, assuming that the CO_2 from anaerobic digestion is transformed into methane and that the CO_2 from the other conversion processes is transformed into either methane or methanol. Methane is a suitable product for CO_2 from anaerobic digestion since it enables the use of CO_2 without separating it from the biogas. The transformation product of CO_2 from the other conversion processes is less determined, but methane and methanol are interesting candidates (the arguments are presented in the introduction of Section 3).

The *technical potential* production of chemicals based on current streams of biogenic CO_2 is estimated to 6.2 EJ of methane, assuming all the available CO_2 is converted into methane, or alternatively to a combination of 4.6 EJ of methanol and 0.4 EJ of methane. The estimated potential production of methane from biogenic CO_2 corresponds to about one third of the current use of fossil methane in Europe (i.e. natural gas, see Box 1). The estimated potential production of methanol is five times larger than the current use of methanol in Europe. Most of the potential production lies in utilising CO_2 from biomass combustion and waste incineration. The utilisation of CO_2 from anaerobic digestion would enable the production of 0.4 EJ of methane, i.e. a 60% increase of the current biogas production. The *economic potential* is likely to be considerably smaller and probably exclude for example biomass combustion plants below a certain size for which CO_2 capture is unlikely to be viable.

Realising the technical potential production of chemicals from biogenic CO_2 is estimated to require 3200 TWh of electricity, assuming methane is the end product, and 2500 TWh of electricity assuming methanol is the main product. These estimates are based on an efficiency of 70% for water electrolysis. Assuming a development towards 90% electricity-to-hydrogen efficiency, the electricity requirements could decrease by up to 32%. For comparison, total electricity production in OECD Europe amounted to 3545 TWh in 2015 (IEA, 2016). Hence, realising the technical potential production of chemicals implies an enormous expansion of renewable electricity production.

The *technical potential* production of chemicals from biogenic CO_2 will be considerably larger in the future assuming an increased use of biomass and that most of this is used in large combustion plants. Assuming a future biomass use of 12 EJ and that most of this is used in large combustion plants (see combustion allocation scenario presented in Section 5.1), the potential production of CO_2-based chemicals amounts to 15.3 EJ of methane or alternatively to 1.3 EJ of methane and 11 EJ of methanol. The required electricity for this is estimated to 8000 TWh and 6200 TWh, respectively.

Table 8: The estimated potential production of CO_2-derived methane or combination of methane and methanol based on the biogenic CO_2 available in OECD Europe in 2014 (see Table 3) and the estimated electricity input that would be required for both combinations.

Biomass conversion process	**Biomass use (PJ/y)**	**CO_2 (Mt/yr)**	**Potential production of CO_2-based chemicals (PJ/yr)**		**Electricity input[c] (TWh/yr)**	
			Methane[a] route	**Methanol[b] & methane route**	**Methane route**	**Methanol & methane route**
Combustion	2870	287	4462	3513 PJ MeOH	2320[d]	1756[d]
Waste incineration	570	81	1259	991 PJ MeOH	655	495
Anaerobic digestion	900	23	397	397 PJ methane	201	201
Fermentation	220	4	76	60 PJ MeOH	38	29
Total	4560	395	6194 PJ methane	4564 PJ MeOH & 397 PJ methane	3214	2481

[a] Assuming methane production via CO_2 methanation and 5% CO_2 conversion losses, which leads to a production of 17.2 PJ of methane per Mt of CO_2.

[b] Assuming methanol production via CO_2 hydrogenation and methanol synthesis and 5% CO_2 conversion losses, which leads to a production of 13.6 PJ of methanol per Mt of CO_2.

[c] Includes the electricity used for electrolysis (assuming water electrolysis with 70% efficiency) and for carbon capture (small electricity consumption in comparison with electrolysis).

[d] 64 TWh of this is used for CO_2 capture.

Table 9: The estimated potential production of CO_2-derived methane or combination of methane and methanol assuming a future annual biomass use of 12 EJ and the estimated electricity input that would be required for both combinations.

Biomass conversion process	**Biomass use (PJ/y)**	**CO_2 (Mt/yr)**	**Potential production of CO_2-based chemicals (EJ/yr)**		**Electricity input[c] (TWh/yr)**	
			Methane[a] route	**Methanol[b] & methane route**	**Methane route**	**Methanol & methane route**
Combustion	9.0	900	14.0	11.0 EJ MeOH	7300[d]	5500[d]
Anaerobic digestion	3.0	77	1.3	1.3 EJ methane	700	700
Total	12.0	977	15.3 EJ methane	11.0 EJ MeOH & 1.3 EJ methane	8000	6200

[a] Assuming methane production via CO_2 methanation and 5% CO_2 conversion losses, which leads to a production of 17.2 PJ of methane per Mt of CO_2.

[b] Assuming methanol production via CO_2 hydrogenation and methanol synthesis and 5% CO_2 conversion losses, which leads to a production of 13.6 PJ of methanol per Mt of CO_2.

[c] Includes the electricity used for electrolysis (assuming water electrolysis with 70% efficiency) and for carbon capture (small electricity consumption in comparison with electrolysis).

[d] 202 TWh of this is used for CO_2 capture.

5.5 SWOT analysis

The conditions for utilisation of biogenic CO_2 vary depending on the source of the CO_2. Based on the material presented previously in this report it is possible to identify a number of important strengths, weaknesses, threats and opportunities associated with the utilisation of CO_2 from different biomass conversion processes (see Table 1). The varying conditions mirror differences concerning primarily the diffusion and maturity of the biomass conversion technology (and thus availability of CO_2) and the requirements of CO_2 separation technology and its maturity.

Table 10: SWOT analysis concerning the potential utilisation of CO_2 from different biomass conversion processes.

	Combustion	**Thermal gasification**	**Anaerobic digestion**	**Fermentation**
Strengths	The current CO_2 volume is large. Biomass combustion is a mature technology.	CO_2 separation is not necessary.	CO_2 separation is not required if the end product is methane. CO_2 separation is currently applied at many biogas plants. Anaerobic digestion is a mature and advantageous technology for management of wet organic waste.	Gas stream with almost 100% CO_2. CO_2 separation is currently applied at a number of ethanol plants. Fermentation of starch and sugar-based crops is a mature technology.
Weaknesses	CO_2 capture from combustion systems is still at demonstration stage. High energy demand for post-CO_2 capture using amine scrubber. The high costs and scale economy of CO_2 capture (many biomass combustion plants are relatively small).	Currently very small CO_2 volume since biomass gasification is not applied at commercial scale. High requirements on cleaning of the producer gas in order not to deactivate catalysts in downstream processes.	The current CO_2 volume is fairly small.	The current CO_2 volume is very small.
Threats	More dynamic operation of CHP and power plants in the future would make CO_2 capture more expensive. Increased competition for biomass could reduce biomass combustion in the future.	Uncertain if and when biomass gasification becomes viable.	The small size of many anaerobic digestion plants could pose an economic barrier to CCU.	The food vs fuel debate could lead to lower European ethanol production from starch and sugar crops in the future.
Opportunities	Can piggyback on the technical development of carbon capture from other applications.	Large technical potential for thermal gasification since it is compatible with nearly all biomass raw materials. Gasification offers high fuel/chemical yield.	Ongoing demonstration projects of methanisation of biogas or CO_2 from anaerobic digestion.	The development of ethanol production from cellulosic biomass could lead to increased ethanol production in the future.

6 Concluding discussion

This report explores the opportunities to produce chemicals and fuels from electricity and biogenic CO_2 in a European context. The studied biomass conversion processes include centralised biomass combustion, waste incineration, anaerobic digestion, fermentation and thermal gasification. A variety of chemicals can be produced via hydrogenation of CO_2. This report focuses on the production of methane and methanol which are widely used in the chemical industry and as fuel. Moreover, methane is the main component of biogas and thus a suitable product of CO_2 from anaerobic digestion.

6.1 Key processes and technologies

The key processes and technologies for utilisation of biogenic CO_2 and electricity for production of chemicals and fuels include water electrolysis and CO_2-based synthesis of methanol and methane. CO_2 separation technologies are also important but not necessary in all process routes. Low-temperature alkaline electrolysis is a robust and widely spread technology for hydrogen production. The SOEC is still at the stage of research and development, but expected to become the most efficient and competitive technology in the future. The SOEC involves high-temperature electrolysis which can be carried out with high electricity-two-hydrogen efficiency if there is access to high-temperature heat. A downside with this technology is that it should be operated continuously and is thus somewhat less flexible.

To what extent CO_2 separation is required differs between the biomass conversion processes. In the case of anaerobic digestion and thermal gasification, it is possible to utilise the CO_2 without separating it from the biogas and producer gas, respectively. Methane production involves the use of either catalytic or biological methanation of CO_2. The technical readiness of catalytic methanation is high and this technology is probably the most suitable process in large-scale applications. Biological methanation, on the other hand, is more flexible with regard to process conditions and suitable in small-scale applications such as utilisation of CO_2 from anaerobic digestion. Methanol can be produced from CO_2 in a one-step or two-step process. The technical readiness is high in both cases.

Regardless of process route, the electrolyser efficiency is a key parameter to the overall energy efficiency. Heat integration between different process units is also important in order to achieve high total energy efficiency, especially if using a SOEC. The analyses in this report rely on an underlying assumption of co-location of the different processes of a process route. It would, however, also be possible to separate the CO_2 and then transport it to another location for utilisation. The production of chemicals could then be supplied by CO_2 from several sources.

6.2 Total generation of CO_2 and technical potential

The *total generation of CO_2* from the current centralised use of biomass and waste in Europe is estimated to 395 Mt CO_2. Most of this CO_2 originates from biomass combustion (287 Mt) and waste incineration (81 Mt). The CO_2 generation in biogas production is estimated to 23 Mt and that from ethanol production to 4.4 Mt. The estimated generation of CO_2 corresponds to about twice the CO_2 needed to cover the annual production of plastics in the EU.

The *technical potential* production of chemicals based on current streams of biogenic CO_2 is estimated to 6.2 EJ of methane, assuming all the CO_2 is converted into methane, or alternatively to a combination of 4.6 EJ of methanol and 0.4 EJ of methane. The estimated potential production of methane or methanol corresponds to about one third of the current use of fossil methane (i.e. natural gas) in Europe or alternatively five times the current use of methanol in Europe. Hence, the use of biogenic CO_2 and electricity can make and important contribution to the production of chemicals and fuels from non-fossil resources. The *economic potential* is likely to be considerably smaller and exclude for example biomass combustion plants below a certain size for which CO_2 capture will not be viable. Realising the technical potential production of chemicals from current streams of biogenic CO_2 is estimated to require 3200 TWh of electricity, assuming methane is the end product, and 2500 TWh assuming methanol is the main product. Hence, realising the technical potential production of chemicals implies an enormous expansion of renewable electricity production in order to supply the required volume of low-carbon electricity.

The biomass use is likely to increase in the future and various resource assessments indicate that it is possible to increase the supply of biomass in Europe. Assuming a doubling of the biomass use to 12 EJ/yr and that most of this is used in centralised combustion plants would increase the potential production of CO_2-based chemicals to 15.3 EJ of methane or alternatively to 1.3 EJ on methane and 11 EJ of methanol. The required electricity for this is estimated to 8000 TWh or 6200 TWh, respectively.

6.3 Main cost driver and production cost

The *main cost driver* for CO_2 utilisation is the cost of electrolysis which is largely independent of the biomass conversion process. The cost of electrolysis is normally dominated by the cost of electricity. An exception to this would be if the electrolyser is only operated when electricity prices are very low, and thus few hours per year. In this case, the capital cost of the electrolyser could exceed the electricity cost. The cost of CO_2 capture is the second most important cost driver for the utilisation of CO_2 from biomass combustion and something that makes this route more costly than others.

The *production cost* of methanol from electricity and biogenic CO_2 in flue gases is estimated to about €780/t methanol in this report when including the main process steps and assuming an electricity price of €50/MWh. The production of methanol from CO_2 and electricity can under most circumstances not meet the current market price of methanol which is set by the production based on natural gas or other fossil feedstocks. The competitiveness of CO_2-based methanol and methane is thus largely dependent on the cost relation between electricity and fossil feedstocks.

6.4 Most promising process routes

Although this report does not present an exhaustive comparative assessment of different process routes, the analyses in this report still make it possible to say something on the most promising process routes. The most promising process routes in the short-term perspective are to utilise CO_2 from anaerobic digestion or fermentation for production of methane or methanol. A major strength of these routes is the high technical readiness. CO_2 separation is currently applied at a large number of fermentation and biogas plants. Furthermore, there are a number of power-to-gas demonstration plants in Europe that produces methane from CO_2 in biogas. Methanol synthesis from CO_2 is also at demonstration scale, but so far these plants use CO_2 from other sources (e.g. geothermal steam) than biomass conversion. The current CO_2 volumes from anaerobic digestion and fermentation are, however, comparatively small.

The currently largest CO_2 volumes are found in biomass combustion. The technical readiness is, however, lower for utilising this CO_2 than for the previously mentioned options. The large investments required for post CO_2 separation or oxyfuel combustion also pose a barrier. Oxyfuel combustion could, however, become an interesting route in the medium and long term.

Biomass gasification with integrated CO_2 hydrogenation is the most promising process route for the medium term assuming biomass gasification can overcome its technical and economic barriers and reach commercial scale. Chemical and fuel synthesis via biomass gasification is associated with comparatively high energy efficiencies and the opportunity not having to separate the CO_2 from the producer gas. This route offers large technical potential since the gasification technology is compatible with most biomass feedstocks.

6.5 Future outlook

The use of fossil fuels must be phased out during the next few decades in order to meet the adopted 2°C target. This transition will make it increasingly important to economise on the biomass carbon since biomass is a limited resource. The transition to non-fossil resources implies a considerable expansion in the use of renewable resources, especially wind and solar energy, but also of biomass for production of chemicals and transportation fuels. The utilisation of biogenic CO_2 and electricity offers a means of utilising the biomass carbon more efficiently, thus increasing the potential production of chemicals and fuels from non-fossil resources substantially.

The transition to non-fossil resources will require the implementation of stronger climate or renewable energy policies. Such policies would benefit the production of CO_2-based chemicals and fuels by increasing the cost of fossil feedstock in relation to electricity. Technical development of electrolysis is also expected to improve the competitiveness of CO_2-based chemical and fuels by reducing the cost of hydrogen production. Future use of biogenic CO_2 and electricity for production of chemicals and fuels will furthermore be influenced by how the use of biomass and its conversion technologies develop. Utilisation of biogenic CO_2 is likely to first be implemented at anaerobic digestion plants. The largest technical potential, however, lies in the CO_2 from biomass combustion or thermal gasification, assuming it can overcome its technical and economic or barriers and reach commercial scale. Biomass gasification with integrated CO_2 utilisation is the most promising process route in the medium term since it offers high technical potential and does not require CO_2 separation.

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8 Appendix

The most important chemical reactions in this report are shown below with their mass and energy balances. The energy balances are based on lower heating values.

Water electrolysis (R1)

$$2\,H_2O \rightharpoonup 2\,H_2 + O_2$$

0	484	0	kJ/mol
36	4	32	g/mol

CO_2 methanation (R3)

$$CO_2 + 4H_2 \rightharpoonup CH_4 + 2H_2O$$

0	968	800	0	kJ/mol
44	8	16	36	g/mol

Methane production via co-electrolysis and CO methanation (R5)

$$CO_2 + 3H_2O \rightharpoonup 3\,H_2 + CO + 2O_2 \rightharpoonup CH_4 + H_2O + 2O_2$$

0		726	393		800	0		kJ/mol
44	54	6	28	64	16	18	64	g/mol

Methanol synthesis (R6)

$$CO_2 + 3H_2 \rightharpoonup CH_3OH\ (l) + H_2O$$

0	726	630	0	kJ/mol
44	6	32	18	g/mol