

---

This is an electronic reprint of the original article.  
This reprint may differ from the original in pagination and typographic detail.

Kajaste-Rudnitskaja, Raili; Hurme, Markku; Oinas, Pekka

## Methanol-Managing greenhouse gas emissions in the production chain by optimizing the resource base

*Published in:*  
AIMS Energy

*DOI:*  
[10.3934/energy.2018.6.1074](https://doi.org/10.3934/energy.2018.6.1074)

Published: 01/01/2018

*Document Version*  
Publisher's PDF, also known as Version of record

*Published under the following license:*  
CC BY

*Please cite the original version:*  
Kajaste-Rudnitskaja, R., Hurme, M., & Oinas, P. (2018). Methanol-Managing greenhouse gas emissions in the production chain by optimizing the resource base. *AIMS Energy*, 6(6), 1074-1102.  
<https://doi.org/10.3934/energy.2018.6.1074>

---

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

*Research article*

## **Methanol-Managing greenhouse gas emissions in the production chain by optimizing the resource base**

**Raili Kajaste\*, Markku Hurme and Pekka Oinas**

Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Finland

\* **Correspondence:** Email: [raili.kajaste@aalto.fi](mailto:raili.kajaste@aalto.fi); Tel: +358405403418.

**Abstract:** The growing demand for methanol as fuel and global competition for resources are key drivers behind the need to find new routes for the production of bulk chemicals such as methanol. Widening the resource base is also linked to the increasing concentrations of methane in the atmosphere. Furthermore, managing greenhouse gas emissions is vital in developing new technologies. This paper compares production routes for methanol based on a cradle-to-gate life cycle assessment (LCA). The LCA is limited to the impact categories of global warming potential (GWP<sub>100</sub>) and energy use. The highest GWP<sub>100</sub> value of 2.97 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH is for methanol from coal, and the lowest, negative emission of 0.99 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH is for methanol in co-production with renewable corn ethanol. A comparison of production routes is performed using the carbon dioxide equivalent abatement cost, and the production cost of methanol. The best performing technology on both production cost and GWP<sub>100</sub> is methanol produced by gasification from wood biomass. The factors affecting the results are addressed.

**Keywords:** methanol; greenhouse gases; resource base; renewable resources; circular economy

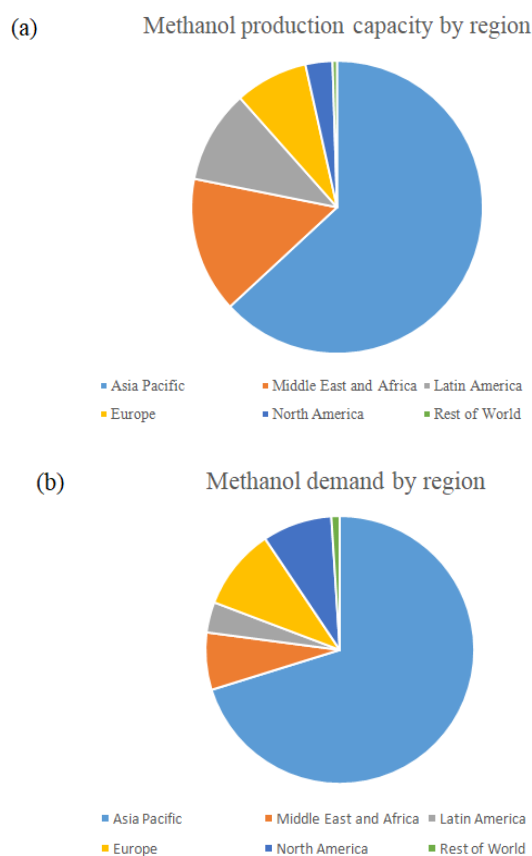
---

**Abbreviations:** ALCA: attributional life cycle assessment; APR: aqueous-phase reforming; ASU: air separation unit; CCU: carbon capture and utilization; CCS: carbon capture and storage; CGE: cold gas efficiency; CO<sub>2</sub>eq: carbon dioxide equivalent; CRF: capital recovery factor; DGS: distillers grains and soluble; FT: Fischer-Tropsch; GHG: greenhouse gases; GWP<sub>100</sub>: global warming potential; HHV: higher heating value; LCA: life cycle assessment; LCI: life cycle inventory; LHV: lower heating value; LNG: liquefied natural gas; MTO: methanol-to-olefins; NG: natural gas; NMVOC:

non-methane volatile organic compounds; PEBG: pressurized entrained biomass gasification; PPM: pulp and paper mill; RWGS: reverse water gas shift; WGS: water gas shift; wt.%: weight percent

## 1. Introduction

Global competition for resources and increasing population, especially in the developing countries, are the trends behind the need to more actively develop technological processes which balance greenhouse gas emissions (GHG), increase the use of renewable resources, and boost the circular economy in the production of bulk chemicals. One of these chemicals is methanol, with a current production rate of 95 million metric tons per year [1]. China dominates the global production and consumption of methanol with over 50%. China is included in Asia Pacific in Figure 1a,b. The demand for methanol has shown significant growth in recent years, resulting in over 100% growth of global production between 2005 and 2016. This growth in demand has mainly originated from the increased use of methanol as fuel and raw material for methanol-to-olefins (MTO) plants [2]. In spite of the globally distributed production, every day 80000 metric tons of methanol is shipped long distances, adding to its environmental load. In 2015, both China and the US imported 5 million metric tons of methanol. The key exporters of methanol are located in the Middle East and in Latin America [3,4].



**Figure 1.** (a) World methanol production capacity of 110 million metric tons by region in % in 2018 [3]; (b) World methanol demand of 90 million metric tons by region in % in 2018 [4].

The global importance of methanol is widely recognized and several studies have assessed its use as both marine and land-based transport fuel [5] and platform chemical [6] as well as power storage media [1]. This has increased the research on both synthesis gas generation and methanol synthesis. A low carbon resource base and renewable energy options are possibilities for finding feasible solutions to replace the traditional production routes of methanol.

Earlier research in the 1980s and 1990s concentrated mainly on optimizing the mass and heat balance of the conventional methanol production routes. The traditional feedstock for methanol synthesis is fossil natural gas transformed into synthesis gas prior to the actual synthesis of methanol. In addition, especially in China, the coal gasification route for producing synthesis gas is widely in use. Coke oven gas and shale gas are also fossil resource based raw materials that are used for the synthesis gas route to methanol. A recent comparison of a coke oven gas derived and natural gas based methanol production revealed that the former would be a better alternative in terms of CO<sub>2</sub> emissions [7]. However, all these processes result in fossil GHG emissions, raising the level of both carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) in the atmosphere and thus call for widening the resource base in the production of methanol. The need to widen the resource base is also linked to the increasing concentrations of CH<sub>4</sub> in the atmosphere. Approximately two-thirds of global CH<sub>4</sub> emissions are attributable to anthropogenic activities, offering increasing opportunities for climate change mitigation [8].

Several researchers have studied the kinetics and technological solutions to improve the overall yield and thermal efficiency of methanol synthesis. Riaz et al. [9] concluded in their review that fluidized bed reactors, membrane reactors and thermally coupled reactors are promising solutions to improve the yield of methanol.

Carbon capture and utilization (CCU) is gaining more support than the earlier promoted carbon capture and storage (CCS). This has also made the exhaust gases of power stations potential sources of raw material for the new methanol synthesis units based on CO<sub>2</sub> and hydrogen (H<sub>2</sub>). The Lurgi/Air Liquide methanol technology is the most advanced with a potential of daily operating capacity of up to 5000 tons [1,6]. Anicic et al. [10] compared the direct synthesis of methanol from CO<sub>2</sub> and H<sub>2</sub> with a reverse water gas shift (RWGS) reaction and subsequent methanol synthesis. Their modelling results indicated that direct methanol synthesis in terms of energy and economic efficiency is more favourable than the RWGS route. An adiabatic RWGS reactor prior to methanol synthesis as in [1] favourably prevents catalyst deactivation. CO<sub>2</sub> capture from the ambient air for methanol synthesis is also an option [11].

The lower than 30% conversion rates of single pass reactors have raised interest in different polygeneration and looping systems for methanol synthesis [12]. In addition, various oxy-fuel technologies in power generation are suitable for combined power and methanol production [13]. The fossil CH<sub>4</sub> emissions of methanol production can be considerably reduced by utilizing tri-reforming technology, combining the CO<sub>2</sub> in flue stack gases with CH<sub>4</sub> as a feed stream [14]. A combination of power stations and methanol plants using natural or synthetic based CH<sub>4</sub> is also possible in the catalytic tri-reforming process using CO<sub>2</sub> reforming, steam reforming and partial oxidation in the production of methanol. Minutillo and Perna [15] found this to be the most suitable for flue gases from a steam cycle power plant with low oxygen concentrations.

In addition to distiller grains and solubles (DGS), renewable fuel processes, such as in a corn ethanol production facility, also produce CO<sub>2</sub> as a by-product which similarly can be utilized for methanol production in direct synthesis with H<sub>2</sub>. Matzen and Demirel [16] assessed the

environmental impacts of this production route using a life cycle assessment (LCA) with an economic allocation for CO<sub>2</sub> and direct impacts of electrolysis for H<sub>2</sub>.

Research on the gasification of biomass for the synthesis gas route to methanol is extensive. In flexible integrated gasification polygeneration facilities producing either electricity or chemicals from coal and wood pellets, methanol production considerably reduces the CO<sub>2</sub> in flue gas streams. When the biomass fraction in the feed exceeds 40% on the energy basis, the production has been considered CO<sub>2</sub> neutral [17]. Van Rens et al. [18] compared the production of methanol, dimethylether and hydrogen from a wood mixture of 10.4% bark, 14.8% wood chips and the remaining tops and branches. Methanol achieved the highest efficiency of production. Melin et al. [19] compared stand-alone methanol and ethanol production with combined production of both from softwood pine loggings. The study was further developed to cover separate lignin and carbohydrate processing for methanol and methane production [20]. The water content of biomass increases the energy demand. Pre-treatment of biomass with torrefaction improves the overall energy economy of methanol production [21].

Different technological choices and process integration in production clusters offer possibilities to improve the feasibility of methanol production from biomass. Holmgren et al. [22,23] concluded that heat integration in particular is a critical factor, and the magnitude of the GHG emissions reductions is dependent upon the reference energy systems and associated emission factors. One of the potential platforms for the production of methanol is a pulp and paper mill (PPM). Andersson et al. [24] modelled methanol production in an existing PPM using a pressurized entrained biomass gasification unit for the generation of the synthesis gas (syngas).

Various side-streams and by-products need valorization to improve the overall feasibility of biodiesel produced by the transesterification of fatty acids, for instance. The reforming of the by-product glycerol to syngas suitable for methanol synthesis has been widely studied. Up to 0.270 kg methanol/kg glycerol can be obtained from the syngas produced by supercritical water reforming with an overall energy efficiency of 38.0%. In addition, a sequestration rate of 0.38 kg CO<sub>2</sub>/kg of glycerol is possible [25].

Thermal integration analysis enables the identification of the possibilities for improving the efficiency of production chains. Bludowsky et al. [26] compared a conventional high temperature biomass gasification process and an aqueous-phase reforming (APR) scheme to produce the syngas stream for methanol synthesis. The latter requires an RWGS unit prior to the methanol synthesis, and had an external energy demand of over 55% higher than that of the biomass gasification process. The carbon balance of both processes showed over 50% carbon losses. The biomass feedstock was modelled as a pure glucose thus reducing the value of the results to an indicative theoretical level.

Solar energy pathways to produce methanol are currently considered unfeasible options. There are several reasons for this: (1) solar energy as a renewable electricity source for H<sub>2</sub> production would require large solar ponds to collect the solar energy [27]; (2) large amounts of water would be required in regions which suffer from water shortages [28]; (3) solar gasification of biomass has been assessed as not competitive with the coal-based methanol production technologies [29]. Moreover, the design of large-scale solar thermochemical reactors is challenging and no commercial applications are foreseen in the near future.

The production of syngas by gasification from different resources including biomass, direct captured CO<sub>2</sub> and polygeneration systems have dominated the research on methanol during the last two decades. An overview of different future options can, for example, be found in Bertau et al. [30].

Less attention has been focused on how to optimize the resource base and technological solutions in terms of greenhouse gas (GHG) emissions, and how to implement circular economy approaches in the production of methanol. This paper compares different emerging possibilities to widen the current resource base of conventional methanol production technologies and analyses the overall GHG emissions utilizing life cycle assessment.

## 2. Methods

The aim of this study is to compare the life cycle GHG balance of methanol produced from different resources and technological combinations on a cradle-to-gate basis. The final use of methanol as a chemical or transport fuel is not included because of the various possible end uses.

Life cycle assessment (LCA) is used to assess the amount of GHG expressed in carbon dioxide equivalents (CO<sub>2</sub>eq), and for the comparison of different methanol processes included in the study. LCA is a common standardized tool [31,32] used for the environmental assessment of fuels and chemicals [5,33]. A GHG management matrix developed by one of the authors [34] is used as an additional tool to help the screening of reviewed studies, and for the scoping of LCA. The reference base case is the production of methanol from coal as a feedstock.

The selected method is that of attributional LCA (ALCA) on a cradle-to-gate basis, reflecting the production systems as described in the references. Any use of allocation, either energy or economic, is included. The functional unit considered is 1 kg of methanol produced. The assessment is limited to the impact categories of global warming potential (GWP<sub>100</sub>) and energy use. The energy use is estimated based on either life cycle inventory (LCI) results or on the overall efficiency, and the highest value is selected.

In addition, a preliminary evaluation of the carbon dioxide equivalent abatement and methanol production cost estimates are made using a capital recovery factor (CRF) for the first 10 years of investment.  $CRF = i(1 + i)^n / [(1 + i)^n - 1]$ , where  $i$  is the interest rate and  $n$  is the number of annuities received for a 10-year period including 35–40% of the total investment cost for longer lifecycles, depending on the overall payback period of the investment, with 5% and 10% annual discount rates. The avoided amount of CO<sub>2</sub>eq is estimated as the difference between the GWP<sub>100</sub> impact and the lower reference value on an annual basis.

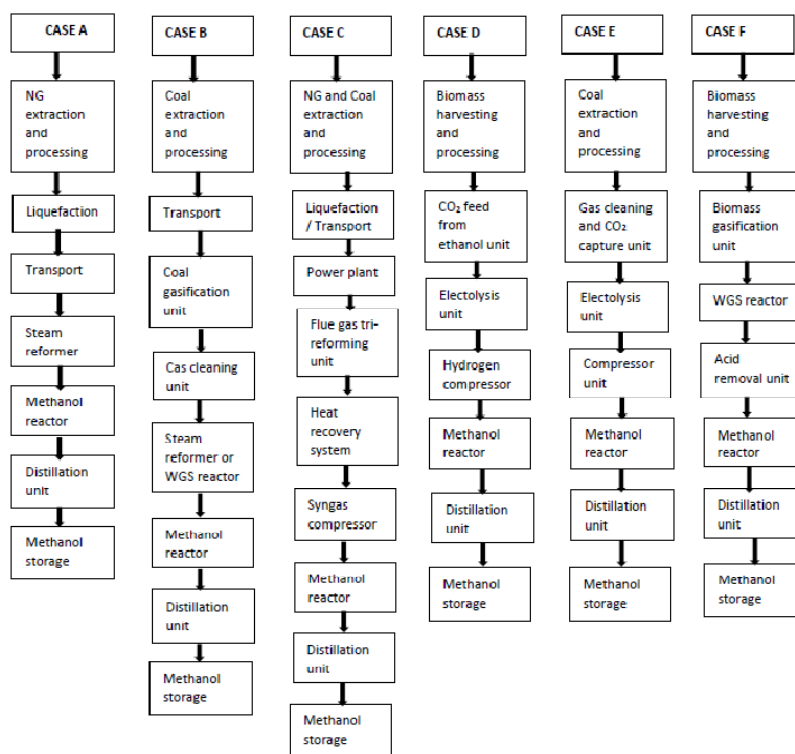
The robustness of key assumptions, uncertainty in the obtained data and sensitivity of the obtained results are assessed, and the limitations of the method used are discussed.

### 2.1. Scope of the study

A review of studies on emerging methanol technologies was made. Six production routes were selected representing both emerging and conventional technologies: (1) fossil methane based [5,35], (2) coal gasification based [21,28], (3) tri-reforming based with power production [15,28,36], (4) in co-production with renewable corn ethanol [16,35], (5) from coal-fired power plant CO<sub>2</sub> and H<sub>2</sub> from electrolysis [1,6], (6) stand-alone wood biomass based [22–24]. The last case includes a sub-case of methanol production from biomass integrated with a PPM [24].

## 2.2. Life cycle inventory data (LCI)

This section briefly describes the production routes of methanol selected for comparison. A simplified flowchart of the six processes is illustrated in Figure 2, and an overview of the methodological choices is shown in Tables 1A–F.

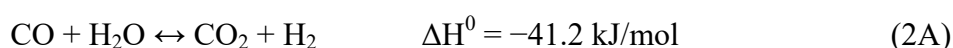
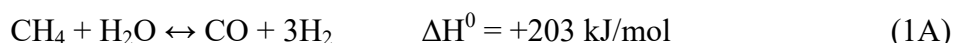


**Figure 2.** A simplified flowchart of the six different methanol production routes.

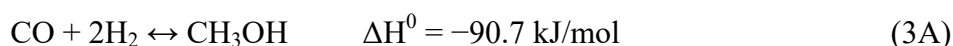
### 2.2.1. Case A—methanol from fossil natural gas

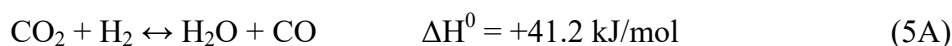
Fossil methane ( $\text{CH}_4$ ) from natural gas and fossil hydrogen ( $\text{H}_2$ ) produced by the steam reforming of  $\text{CH}_4$  are the raw materials used in this traditional process. The LCA inventory data for this methanol production is based mainly on Matzen et al. [35], Brynolf et al. [5] and Minutillo and Perna [15,36].

The key reactions for the steam reforming of natural gas are:



The key reactions for methanol production from synthesis gas, including the reverse water gas shift (RWGS) reaction, are:





The key process units include a steam reformer, a methanol reactor and a raw methanol distillation unit.

The feedstock is average natural gas (NG) extracted in Norway and transported 648 km to the production site of methanol located in Sweden. The methanol production efficiency at the lower heating value (LHV) is 66% and the purity of the final product is over 99% [5]. Norwegian electricity mix is used for the NG extraction and preprocessing, and the average Swedish electricity mix is used for the methanol production site [5]. The methodological choices for this case are shown in Table 1A.

**Table 1A.** Methodological choices for Case A.

Investigated options	Natural gas (NG) extracted and preprocessed in Norway. Liquefied natural gas (LNG) produced in Algeria for alternate case [28].
Functional unit	1 kg of methanol produced
Time horizon	2010–2020
Geographical boundaries	Norway for NG and Gothenburg, Sweden for methanol production.
System boundaries	The study includes all production steps shown in the flowchart (Figure 2) Manufacturing of capital goods and auxiliary materials are not included.
Allocation	No allocation used.
Impact categories	CO <sub>2</sub> equivalents (CO <sub>2</sub> eq) using global warming potential factors for a 100-year period (GWP <sub>100</sub> ). Energy use.
Included primary pollutants	Carbon dioxide (CO <sub>2</sub> ), carbon monoxide (CO), nitrogen oxides (NO <sub>x</sub> ), nitrous oxide (N <sub>2</sub> O), methane (CH <sub>4</sub> ), non-methane volatile organic compounds (NMVOC).
Limitations	Greenhouse gas emissions connected to land use change are not considered in this study.

### 2.2.2. Case B—methanol from coal gasification

Synthesis gas from coal and fossil hydrogen (H<sub>2</sub>) produced by the steam reforming of CH<sub>4</sub> or by the water gas shift (WGS) reaction are the basic raw materials used in this traditional process. The LCA inventory data for this case of methanol production is based on Matzen et al. [35], Trudewind et al. [28] and Trop et al. [21].

The key summary reaction for coal gasification and the key reaction for water gas shift are:



The key reactions for methanol from synthesis gas are:



The key process units include a coal gasification unit, a gas cleaning unit, a steam reformer or a WGS reactor, a methanol reactor and a raw methanol distillation unit.



Coal is gasified in an entrained flow coal gasifier and the cooled synthesis gas produced is treated for sulphur removal in a Rectisol process. The released heat is used to heat the synthesis gas after desulphurization and to produce low pressure steam. The mixture of low pressure steam and purified syngas is conveyed to the water gas shift (WGS) process. After the WGS reactor, the conditioned gas is ready for the methanol synthesis unit and further purification in the distillation unit. This well-to-tank LCA ends at the methanol storage facility. The mining, coal conditioning and transport chain starts in South Africa. Coal is transported 540 km to the coast by diesel engines, loaded and transported 12,975 km by freight to the port in Rotterdam, the Netherlands, and from there a further 668 km by barge to the gasification plant in Germany. The methanol plant is assumed to be in the same location. The methodological choices for this case are shown in Table 1B.

**Table 1B.** Methodological choices for Case B.

Investigated options	Coal extracted and preprocessed in South Africa
Functional unit	1 kg of methanol produced
Time horizon	2010–2020
Geographical boundaries	Coal production in South Africa, methanol production in Germany.
System boundaries, allocation, impact categories, included primary pollutants and limitations are similar to Case A.	

### 2.2.3. Case C—methanol production by flue gas tri-reforming integrated with power production

Fossil methane (CH<sub>4</sub>), fossil coal, fossil CO<sub>2</sub> and fossil H<sub>2</sub> are the raw materials used in this process. The LCA inventory data for this methanol production utilizing a flue gas stream of a coal-fired/CH<sub>4</sub>-fired power plant, is based mainly on Minutillo and Perna [15,36] and Trudewind et al. [28]. The key reactions for methane tri-reforming are:



The reactions for methanol synthesis are the same as in Case B, i.e. reactions 3B and 4B.

The flue gases from the power plant, which contain N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub>, are used as reactants (reactions 1C, 2C and 3C) to convert the methane into a syngas with the optimal H<sub>2</sub>/CO ratio equal to 2 required for methanol synthesis.

The key process units include a coal-fired power plant, a tri-reforming unit connected to a CH<sub>4</sub>-fired catalytic burner, a heat recovery system, a syngas compressor, a methanol reactor and a distillation unit. For a detailed technical description of the process units, please refer to Minutillo and Perna [15]. The methodological choices for this case are shown in Table 1C.

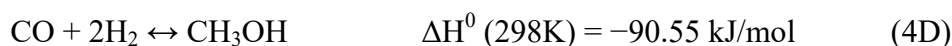
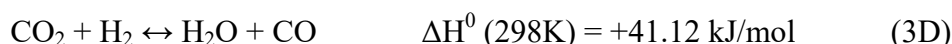
**Table 1C.** Methodological choices for Case C.

Investigated options	NG extracted and preprocessed in Algeria. Coal extracted and preprocessed in Pennsylvania, USA.
Functional unit	1 kg of methanol produced, 1 kWh electricity produced
Time horizon	2010–2020
Geographical boundaries	East coast of the United States of America, Algeria and Italy
System boundaries	The study includes all production steps shown in the flowchart (Figure 2). Manufacturing of capital goods and auxiliary materials are not included. Flue gases from a steam cycle power plant are used for methanol production.
Allocation	Allocation of the emissions between net power and methanol production.
Impact categories, included primary pollutants and limitations are similar to Case A.	

#### 2.2.4. Case D—methanol in co-production with renewable corn ethanol

Biogenic CO<sub>2</sub> and renewable H<sub>2</sub> are the raw materials used in this process. The LCA data for methanol production from a CO<sub>2</sub> side stream of renewable ethanol production is from Matzen and Demirel [16], with the key assumption that economic allocation is used to account for the impact of CO<sub>2</sub> emissions. Each gallon (3.79 litres) of corn ethanol produces 3.08 kg of CO<sub>2</sub> and 2.56 kg of distiller grains and solubles (DGS). Wind power generated electrolytic H<sub>2</sub> data is used for the LCA. The methanol production data is from Matzen et al. [35].

The key reactions for this methanol route are:



The key process units include a wind power driven electrolysis unit for splitting water into hydrogen and oxygen, a hydrogen compressor, a feed system for CO<sub>2</sub> from the corn ethanol unit, a methanol synthesis reactor of Lurgi type and a distillation unit.

Hydrogen for this small-scale methanol synthesis is produced by the wind-powered electrolysis of water. Oxygen is considered as a by-product of electrolysis with an output of 1.530 kg O<sub>2</sub>/kg methanol produced. Wind power is selected because its cost is around 38% lower than that of solar photovoltaic power [35]. CO<sub>2</sub> is recovered as a by-product of renewable ethanol production. The raw material for the ethanol production is dry milled corn. The allocation of environmental load from ethanol production is based on the economic values of ethanol, DGS and CO<sub>2</sub>.

Emissions of the compression and transportation of the CO<sub>2</sub> are assumed to be negligible. The overall energy efficiency for the renewable methanol is around 58%. In addition to methanol, the process produces waste water, flue gas and steam used either for electricity production or for process heat. The flue gas stream contains mostly CO<sub>2</sub>, with less than 0.5% of the produced methanol being lost. The waste water stream contains less than 1% methanol. For a detailed process description, please refer to Matzen and Demirel [16]. The methodological choices for this case are shown in Table 1D.

**Table 1D.** Methodological choices for Case D.

Investigated options	Biomass harvested and preprocessed in Nebraska. CO <sub>2</sub> feed extracted from corn ethanol process unit and methanol produced in southeast Nebraska.
Functional unit	1 kg of methanol produced
Time horizon	2010–2020
Geographical boundaries	Nebraska, United States of America
System boundaries	The study includes all production steps shown in the flowchart (Figure 2) Production and operation of wind power and electrolyser are partially included. Other manufacturing of capital goods and auxiliary materials are not included.
Allocation	Economic allocation used.
Impact categories, included primary pollutants and limitations are similar to Case A.	

### 2.2.5. Case E—methanol from coal power plant CO<sub>2</sub> and H<sub>2</sub> from electrolysis

Fossil CO<sub>2</sub> and renewable H<sub>2</sub> are the raw materials used in this process. The LCA inventory data for methanol production from a purified CO<sub>2</sub> side stream of a coal-fired power station in combination with a wind power driven electrolysis unit is mainly from Matzen et al. [35], Pontzen et al. [6] and Räuchle et al. [1]. The key reactions for this methanol route are:



The key process units include a CO<sub>2</sub> capture unit, an electrolysis unit for H<sub>2</sub> production, a methanol reactor unit and a crude methanol distillation unit.

Overall reductions in CO<sub>2</sub> emissions can only be achieved if the H<sub>2</sub> is produced from renewable resources, i.e. the electrolysis uses solar-, wind- or biomass-based electricity. Räuchle et al. [1] made a detailed analysis of methanol plants by AirLiquide/Lurgi, concluding that the best overall efficiency with renewable H<sub>2</sub> reached 51% (assumed on an LHV basis). H<sub>2</sub> is generated from surplus electric power by electrolysis and recycled CO<sub>2</sub> comes from a CCU unit of the power station. The methodological choices for this case are shown in Table 1E.

**Table 1E.** Methodological choices for Case E.

Investigated options	Coal extracted and preprocessed in Germany. Hydrogen and methanol production in Germany.
Functional unit	1 kg of methanol produced
Time horizon	2010–2020
Geographical boundaries	Germany
Allocation	Allocation of emissions used, power station operational emissions excluded.
System boundaries, impact categories, included primary pollutants and limitations are similar to Case A.	

### 2.2.6. Case F—methanol from wood biomass

This case is a stand-alone methanol production unit from wood biomass. The LCA inventory data is mainly based on Holmgren et al. [22,23], Andersson et al. [24]. The process is similar to that of coal gasification (Case B), except that wood biomass is the feedstock. The synthesis gas from biomass gasification is the basic raw material used in this process. The hydrogen (H<sub>2</sub>) content is adjusted in the water gas shift (WGS) reactor. Additionally, the result is compared with a methanol production unit integrated into an existing pulp and paper mill.

The key reactions for this methanol route are given below.

The key summary reaction for biomass gasification and key reaction for water gas shift are:



The key reactions for methanol from synthesis gas are:



The average wood biomass composition differs from fossil resources in its oxygen content and original humidity of 40–50%. The molecular composition of Nordic softwood pine, (wt.%) of C 53.3, H 6.1, O 41.2, N 0.1, S 0.01, ash 0.7, illustrates the oxygen content well [19].

The key process units include a cryogenic air separation unit (ASU) for oxygen production, a pressurized entrained biomass gasification unit (PEBG), a sulphur tolerant water gas shift (WGS) reactor, an acid removal unit, a methanol synthesis reactor and a distillation unit. The methodological choices for this case are shown in Table 1F.

**Table 1F.** Methodological choices for Case F.

Investigated options	Biomass harvested and preprocessed in Sweden. Electricity produced in Sweden
Functional unit	1 kg of methanol produced
Time horizon	2010–2020
Geographical boundaries	Sweden
System boundaries, allocation, impact categories, included primary pollutants and limitations are similar to Case A.	

The gasification unit includes a biomass rotary drying unit where the biomass is dried to a water content of 8%. The grinding unit reduces the dried biomass to an average particle size between 0.6 and 0.8 mm prior to being fed to pressurized entrained flow biomass gasification (PEBG) with pure oxygen as a gasification agent. The thermal energy input to both the rotary dryer and grinding unit are included and recalculated as electricity in the overall power consumption [24]. The same applies to the cryogenic air separation unit (ASU). Unreacted syngas is recycled to the methanol reactor with a 5% purge.

### 3. Results

This section includes the life cycle inventory results for all six cases. The cradle-to-gate environmental impact analysis covers greenhouse gas emissions shown as GWP<sub>100</sub> impact and energy use. The CRF calculation results for the preliminary carbon dioxide equivalent abatement cost estimation and the methanol production costs are listed in Section 3.3. The uncertainty of results is addressed including the assumptions made, quality of data and limitations arising from the methodology used.

#### 3.1. Life-cycle inventory analysis

The energy and material balances are calculated in a uniform manner using the functional unit of 1 kg methanol (CH<sub>3</sub>OH). The energy use units differ from case to case depending on the original values available for the case. The shown key inputs generate the given key output and related primary pollutants. If a primary pollutant is missing from the table, it indicates that it was not considered in the reference used.

The energy value for methanol used in all calculations is 21.832 MJ/kg methanol [28] located somewhere between the higher heating value (HHV) of 23.8 MJ/kg methanol and the lower heating value (LHV) of 21.1 MJ/kg of methanol used by Minutillo and Perna [15]. The cradle-to-gate energy use for producing methanol is either estimated from LCI tables or from the overall efficiency, and the highest value is chosen.

When available, the GWP<sub>100</sub> impact is given separately for raw material extraction and processing, transport, power production and methanol synthesis. The GWP<sub>100</sub> value is the sum of the carbon dioxide equivalents (CO<sub>2</sub>eq) of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. The summary GWP<sub>100</sub> is listed for the functional unit (1 kg CH<sub>3</sub>OH) using the unit of kg CO<sub>2</sub>eq. The CO<sub>2</sub>eq of CO<sub>2</sub> equals one. The values for CH<sub>4</sub> and N<sub>2</sub>O are calculated as CO<sub>2</sub>eq using the multiplying coefficients of 25 for CH<sub>4</sub> and 298 for N<sub>2</sub>O from the IPCC AR4 report (2007), resulting in the equation: (GWP<sub>100</sub> in kg CO<sub>2</sub>eq = kg CO<sub>2</sub> + (kg CH<sub>4</sub>) × 25 + (kg N<sub>2</sub>O) × 298). In addition to the LCI results listed in Tables 4A–F, alternative cases impacting the GWP<sub>100</sub> results are considered for each case. The inventory results are further compared to the reference base case of methanol from coal as a feedstock.

##### 3.1.1. Case A—methanol from fossil natural gas

The NG extracted in Norway is transported to the production site in Sweden, where syngas is generated by the steam reforming of NG and transformed to methanol, as described in Section 2.2.1. The overall efficiency on an LHV basis is 66%. The GWP<sub>100</sub> for methanol from fossil NG is 0.462 kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use is 11.5 MJ/kg methanol. The inventory results for this case are shown in Table 2A.

An alternative case for the production of methanol is NG extracted in Algeria and transported to a production site in Germany [28]. In this case the GWP<sub>100</sub> for methanol varies from 0.873 to 0.881 kg CO<sub>2</sub>eq/kg methanol (Alternative 1A and 2A in Figure 6). The primary energy demand varies from 33.277 MJ/kg methanol [5] to 37.114 MJ/kg methanol [28], increasing the uncertainty of energy use by over 10 per cent if the latter reference is used.

**Table 2A.** LCI results for methanol from fossil natural gas (Case A).

	Unit	Value	Reference & Notes
<b>Input</b>			
Natural gas (NG)	MJ/kg CH <sub>3</sub> OH	32.748	Brynolf et al. [5]
Crude oil	MJ/kg CH <sub>3</sub> OH	0.524	
Coal	MJ/kg CH <sub>3</sub> OH	0.0024	
Uranium	MJ/kg CH <sub>3</sub> OH	0.0028	
Hydropower	MJ/kg CH <sub>3</sub> OH	0.0006	
Other renewables	MJ/kg CH <sub>3</sub> OH	0.0001	
<b>Output</b>			
Methanol	kg	1	Brynolf et al. [5]
Primary pollutants			
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	0.437	
CO	kg/kg CH <sub>3</sub> OH	0.00014	
NO <sub>x</sub>	kg/kg CH <sub>3</sub> OH	0.001	
N <sub>2</sub> O	kg CO <sub>2</sub> eq	0.0189	
CH <sub>4</sub>	kg CO <sub>2</sub> eq	0.006	
NMVOC* + CH <sub>2</sub> O + C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub>	kg/kg CH <sub>3</sub> OH	0.00039	
GWP <sub>100</sub> for methanol production from NG	kg CO <sub>2</sub> eq	0.462	
Energy use	MJ/kg CH <sub>3</sub> OH	11.446	
<b>Reference value</b>			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

\*NMVOC = non methane volatile organic compounds.

### 3.1.2. Case B—methanol from coal

Methanol from coal is mostly produced in China. However, here we selected coal from South Africa with an LHV of 24.7 MJ/kg [28] and complemented the results with Czech coal from Ledvice with an LHV of 21.73 MJ/kg [21] in the synthesis part. The methanol output is based on 57.7% cold gas efficiency (CGE) where the CGE was calculated using higher heating values (HHV), Trop et al. [21].

The GWP<sub>100</sub> for methanol from coal is 2.965 kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use (without transport fuels) is 22.8 MJ/kg methanol. The inventory results for this case are shown in Table 2B.

Alternatively, the GWP<sub>100</sub> impact of methanol produced by coal gasification can be considerably lowered by replacing 40% [17] to 50% [21] of the coal energy with biomass (Alternative 1B and 2B in Figure 6).

### 3.1.3. Case C—methanol by flue gas tri-reforming integrated with power production

The tri-reforming plant produces 990 MW methanol and 52.3 MW net power, and energy allocation is used to split the emissions between power and methanol production. The electrical efficiency of the coal-fired power plant is 38.6% calculated on an LHV basis [15]. The overall efficiency of the power plant and methanol production is 56% on an LHV basis.

**Table 2B.** LCI results for methanol from coal (Case B).

	Unit	Value	Reference & Notes
Input of coal mining, conditioning and transport			Trudewind et al. [28]
Hard coal, mined and conditioned	kg/kg CH <sub>3</sub> OH	1.672	
Transport, diesel engine	km	541	
Oceanic freight carrier	km	12975	
Barge	km	668	
Electricity demand	MJ/kg CH <sub>3</sub> OH	0.0481	
Input gasification, WGS, methanol production			Trop et al. [21]
Hard coal, mined and conditioned	kg/kg CH <sub>3</sub> OH	1.670	
Electricity demand	MJ/kg CH <sub>3</sub> OH	6.407	
Electricity production	MJ/kg CH <sub>3</sub> OH	3.136	
Output			
Methanol	kg	1	
Primary pollutants of coal mining, conditioning and transport			Trudewind et al. [28]
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	0.367	
NO <sub>x</sub>	kg/kg CH <sub>3</sub> OH	0.00426	
N <sub>2</sub> O	kg CO <sub>2</sub> eq	n.a.	
CH <sub>4</sub>	kg CO <sub>2</sub> eq	0.148	
NMVOC (non-specific)	kg/kg CH <sub>3</sub> OH	0.00731	
GWP <sub>100</sub> for coal mining, conditioning and transport	kg CO <sub>2</sub> eq	0.515	
Primary pollutants gasification, WGS, methanol production			Trop et al. [21]
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	2.45	
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.965	
Energy use	MJ/kg CH <sub>3</sub> OH	22.786	
Reference value			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

The natural gas (NG) composition (molar basis) is: 90.0% CH<sub>4</sub>, 4.4% C<sub>2</sub>H<sub>6</sub>, 0.1% C<sub>3</sub>H<sub>8</sub>, 1.3% CO<sub>2</sub>, 4.3% N<sub>2</sub> [15]. The heating values of NG are 44.8 MJ/kg (LHV) and 49.7 MJ/kg (HHV). The assumption is that the production losses and transport distances for the Pennsylvania Upper coal to Italy do not exceed the values used in Case B. Therefore, the primary pollutants for coal mining, conditioning and transport are calculated based on the reference values of Trudewind et al. [28], and included as upstream primary pollutants for the power production. The natural gas production losses are estimated to be 0.27% for the methanol production amount of NG [37]. The assumption is that NG transport emissions do not exceed the values used by Trudewind et al. [28], where 58% of the methane is transported from Algeria by pipeline and 42% by shipment in LNG freight ships to Europe.

The GWP<sub>100</sub> for methanol by flue gas tri-reforming is 1.392 kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use is 17.7 MJ/kg methanol. The inventory results for this case are shown in Table 2C. Without the allocation of emissions between power and methanol production, the methanol production would be loaded with 0.31 kWh/kg CH<sub>3</sub>OH electricity emissions, meaning additional emissions of 0.961 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH with the given GWP<sub>100</sub> for net power

production (Table 2C). This would increase the total GWP<sub>100</sub> for methanol production by tri-reforming to 2.353 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH (Alternative 1C in Figure 6).

**Table 2C.** LCI results for methanol by tri-reforming integrated with power production (Case C).

	Unit	Value	Reference & Notes
Input power production			Minutillo and Perna [15]
Hard coal, mined and conditioned	MJ/kg CH <sub>3</sub> OH	6.65	
Auxiliary power	MJ/kg CH <sub>3</sub> OH	0.143	
Input tri-reforming and methanol production			Minutillo and Perna [15]
Flue gas from power plant	kg/kg CH <sub>3</sub> OH	2.698	CO <sub>2</sub> 15.7%
Methane (NG)	MJ/kg CH <sub>3</sub> OH	33.961	
Steam	kg/kg CH <sub>3</sub> OH	0.411	
Output			
Net electricity	MJ/kg CH <sub>3</sub> OH	1.191	
Methanol (CH <sub>3</sub> OH)	kg	1	
Primary pollutants power production			
GWP <sub>100</sub> for upstream coal emissions	kg CO <sub>2</sub> eq	0.0831	Trudewind et al. [28]
GWP <sub>100</sub> for upstream NG emissions	kg CO <sub>2</sub> eq	0.2827	Trudewind et al. [28]
GWP <sub>100</sub> for net power production	kg CO <sub>2</sub> /kWh	3.1	Minutillo and Perna [15]
Primary pollutants tri-reforming and methanol production			
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	1.026	Minutillo and Perna [15]
GWP <sub>100</sub> for methanol production by tri-reforming	kg CO <sub>2</sub> eq	1.392	
Energy use	MJ/kg CH <sub>3</sub> OH	17.731	
Reference value			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

#### 3.1.4. Case D—methanol in co-production with renewable corn ethanol

This process produces corn ethanol, DSG and methanol. The methanol is produced from the biogenic CO<sub>2</sub> captured from ethanol production and renewable H<sub>2</sub>, and economic allocation is used to divide the environmental load between ethanol, DSG and biogenic CO<sub>2</sub>.

The GWP<sub>100</sub> for methanol in co-production with corn ethanol and DSG is −0.989 kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use is 15.8 MJ/kg methanol. The inventory results for this case are given in Table 2D.

The economic allocation factor of total production emissions and energy use for CO<sub>2</sub> is 6.1%. This percentage gives a GWP<sub>100</sub> load of 0.0784 kg CO<sub>2</sub>eq/kg CO<sub>2</sub> used for methanol production (Table 2D). If we change this percentage to 100% with the 1.43 kg CO<sub>2</sub> needed for one kg methanol produced, the GWP<sub>100</sub> load from CO<sub>2</sub> production will change to 1.8379 kg CO<sub>2</sub>eq/kg methanol produced. The overall GWP<sub>100</sub> load of methanol production would change from the negative value of −0.989 to 0.8489 kg CO<sub>2</sub>eq/kg methanol produced. This demonstrates the impact of economic allocation on the LCA result for case D.



**Table 2D.** LCI results for methanol in co-production with corn ethanol (Case D).

	Unit	Value	Reference & Notes
Input of chemicals and energy			Matzen et al. [35]
Hydrogen (H <sub>2</sub> )	kg/kg CH <sub>3</sub> OH	0.192	
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	1.43	
Fossil fuel (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)	kWh/kg CH <sub>3</sub> OH	0.950	
Renewable fuel (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)	kWh/kg CH <sub>3</sub> OH	6.175	
Output			
Methanol (CH <sub>3</sub> OH)	kg	1	
Steam	kg/kg CH <sub>3</sub> OH	0.957	
Flue gases	kg/kg CH <sub>3</sub> OH	0.0546	
Waste water	kg/kg CH <sub>3</sub> OH	0.5629	
Primary pollutants (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)			Matzen and Demirel [16]
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	-1.141	negative emission
CO	kg/kg CH <sub>3</sub> OH	$0.2086 \times 10^{-3}$	
NO <sub>x</sub>	kg/kg CH <sub>3</sub> OH	$0.8250 \times 10^{-3}$	
N <sub>2</sub> O	kg/kg CH <sub>3</sub> OH	$0.4216 \times 10^{-3}$	
CH <sub>4</sub>	kg/kg CH <sub>3</sub> OH	$0.2800 \times 10^{-3}$	
NM VOC (non-specific)	kg/kg CH <sub>3</sub> OH	$0.1573 \times 10^{-3}$	
GWP <sub>100</sub> for H <sub>2</sub> production emissions	kg CO <sub>2</sub> eq/kg H <sub>2</sub>	0.1425	
GWP <sub>100</sub> for CO <sub>2</sub> production emissions	kg CO <sub>2</sub> eq/kg CO <sub>2</sub>	0.0784	
GWP <sub>100</sub> for methanol in co-production	kg CO <sub>2</sub> eq	-0.989	negative emission
Energy use (58% efficiency on LHV basis)	MJ/kg CH <sub>3</sub> OH	15.809	
Reference value			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

The GWP<sub>100</sub> value for methanol in co-production with corn ethanol in Table 2D is taken from Matzen and Demirel [16]. If the summary value for CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> is used, the GWP<sub>100</sub> value will change to -1.008 kg CO<sub>2</sub>eq/kg methanol (Alternative 1D in Figure 6).

The hydrogen production by electrolysis has a GHG impact of 0.97 kg CO<sub>2</sub>eq/kg H<sub>2</sub> of which 78% are attributed to wind turbine production and operation. The GWP<sub>100</sub> for H<sub>2</sub> production emissions shown in Table 2D includes 14.7% of these emissions [35]. Including all the H<sub>2</sub> emissions would change the GWP<sub>100</sub> for methanol by 0.159 units from -0.989 to -0.83 (Alternative 2D in Figure 6).

Changing the H<sub>2</sub> production from electrolysis to NG- or coal-based would considerably change the emissions. Starting from NG the emissions are 7.33 kg CO<sub>2</sub>/kg H<sub>2</sub>, and correspondingly from coal 29.33 kg CO<sub>2</sub>/kg H<sub>2</sub> using 75% energy efficiency [35]. The use of biogenic CO<sub>2</sub> and H<sub>2</sub> from NG in methanol production would change the negative GWP<sub>100</sub> value for methanol in Table 2D to a positive value of 0.418 kg CO<sub>2</sub>eq/kg methanol (Alternative 3D in Figure 6). The use of biogenic CO<sub>2</sub> and H<sub>2</sub> from coal would change the negative GWP<sub>100</sub> value for methanol in Table 2D to a positive value of 4.642 kg CO<sub>2</sub>eq/kg methanol (Alternative 4D in Figure 6). This indicates clearly that the results of the LCA are altered drastically by changing the raw material production route or other assumptions.

### 3.1.5. Case E—methanol from captured CO<sub>2</sub> and H<sub>2</sub>

This methanol production route is based on the same type of technology as in Case D with captured CO<sub>2</sub> from a coal-fired power station, and the emissions of power production are excluded from the GHG balance. The overall efficiency of methanol production is assumed to 51% on an LHV basis. The hard coal mining, processing and transport emissions are estimated as in Case B, but include only a short transport distance of 541 km inside Germany. The assumption is that these emissions are a maximum of 10% of the corresponding emissions for Case B, and total 0.052 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH. The emissions of flue gas cleaning, CO<sub>2</sub> CCU unit and methanol synthesis are adapted from Case D, and corrected with the efficiency difference between cases D and E, i.e. by multiplying the corresponding values from Case D by  $58/51 = 1.1373$ .

The GWP<sub>100</sub> for methanol from the captured CO<sub>2</sub> and H<sub>2</sub> is  $-0.752$  kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use is 15.8 MJ/kg methanol. The inventory results for this case are shown in Table 2E.

The negative GWP<sub>100</sub> for methanol production derives from the capture of fossil CO<sub>2</sub> and the use of renewable wind power for the production of H<sub>2</sub>.

Fossil CO<sub>2</sub> can be replaced by renewable CO<sub>2</sub> from a biomass-fired power station. This would further increase the biogenic carbon capture and enforce the negative value of GWP<sub>100</sub> for methanol production. The replacement of renewable H<sub>2</sub> with fossil H<sub>2</sub> generated from natural gas (NG) or by gasification of coal would change the overall GWP<sub>100</sub> for methanol as shown in Case D.

Similarly, a different source, i.e. the electrolysis of water, increases the overall GWP<sub>100</sub> for methanol. Electricity from the grid would increase the GWP<sub>100</sub> for methanol by 3.933 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH with the average electricity emissions of 0.56 kg CO<sub>2</sub>eq/kWh in Germany [38]. For Case E, this would change the initially negative overall emissions to a positive load of 3.181 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH (Alternative 2E in Figure 6) exceeding even the value for Case B.

The methanol plant could also be located inside a petroleum refinery complex and utilize the H<sub>2</sub> produced by the refinery. The impact of the CO<sub>2</sub> stream would remain unchanged compared to Case E, and the H<sub>2</sub> stream would increase the GWP<sub>100</sub> for methanol by 2.82 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH. For Case E this would change the overall GWP<sub>100</sub> for methanol to 2.068 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH (Alternative 1E in Figure 6). The H<sub>2</sub> emissions produced by the petroleum refinery are based on Moretti et al. [39].

**Table 2E.** LCI results for methanol from captured CO<sub>2</sub> and H<sub>2</sub> (Case E).

	Unit	Value	Reference & Notes
Input of coal mining, conditioning and transport			Trudewind et al. [28]
Hard coal, mined and conditioned	kg	1.672	
Transport, diesel engine	km	541	
Input of chemicals and energy			
Hydrogen (H <sub>2</sub> )	kg/kg CH <sub>3</sub> OH	0.218	
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	1.626	
Fossil fuel (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)	kWh/kg CH <sub>3</sub> OH	1.080	
Renewable fuel (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)	kWh/kg CH <sub>3</sub> OH	7.023	

*Continued on next page*

	Unit	Value	Reference & Notes
Output			
Methanol (CH <sub>3</sub> OH)	kg	1	
Steam	kg/kg CH <sub>3</sub> OH	1.088	
Flue gases	kg/kg CH <sub>3</sub> OH	0.0621	
Waste water	kg/kg CH <sub>3</sub> OH	0.6402	
Primary pollutants of coal mining, processing and transport			Trudewind et al. [28]
CO <sub>2</sub>	kg	0.0367	
CH <sub>4</sub>	kg CO <sub>2</sub> eq	0.0148	
Primary pollutants (H <sub>2</sub> + CO <sub>2</sub> + CH <sub>3</sub> OH production)			Matzen and Demirel [16]
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	-0.9843	negative emission
CO	kg/kg CH <sub>3</sub> OH	0.2372 × 10 <sup>-3</sup>	
NO <sub>x</sub>	kg/kg CH <sub>3</sub> OH	0.9282 × 10 <sup>-3</sup>	
N <sub>2</sub> O	kg/kg CH <sub>3</sub> OH	0.4795 × 10 <sup>-3</sup>	
CH <sub>4</sub>	kg/kg CH <sub>3</sub> OH	0.3184 × 10 <sup>-3</sup>	
NM VOC (non-specific)	kg/kg CH <sub>3</sub> OH	0.1789 × 10 <sup>-3</sup>	
GWP <sub>100</sub> for input coal	kg CO <sub>2</sub> eq	0.052	
GWP <sub>100</sub> for H <sub>2</sub> production emissions	kg CO <sub>2</sub> eq/kg H <sub>2</sub>	0.1621	
GWP <sub>100</sub> for CO <sub>2</sub> production emissions	kg CO <sub>2</sub> eq/kg CO <sub>2</sub>	0.0892	
GWP <sub>100</sub> for methanol production from CO <sub>2</sub> + H <sub>2</sub>	kg CO <sub>2</sub> eq	-0.752	negative emission
Energy use (51% efficiency on LHV)	MJ/kg CH <sub>3</sub> OH	20.976	
Reference value			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

### 3.1.6. Case F—methanol from renewable wood biomass

This process uses 338 MW wood biomass input with 8% humidity and 41 MW external electricity to produce 187 MW methanol and 55 MW district heat. The moisture content of the harvested wood biomass is assumed to be 40%. The biomass-to-methanol overall efficiency is 55.3% assumed on an LHV basis [24].

The GWP<sub>100</sub> for biomass harvesting is assumed to be 3.89 g CO<sub>2</sub>eq/MJ biomass including the transport emissions to and inside the production site [20]. The transport distance is assumed to be max. 400 km. The electricity emissions are assumed to be 12.78 g CO<sub>2</sub>eq/MJ electricity from the Swedish grid [38]. The biomass heating value is assumed to be 12.68 MJ/kg on an LHV basis with a moisture content of 40%. The sulphur recovered in the Claus recovery unit was neither included in the efficiency calculations nor in the GWP<sub>100</sub> impact. The actual methanol synthesis emissions are adapted from Trop et al. [21], and corrected to 55.3% efficiency from the 57.7% used for Case B.

The GWP<sub>100</sub> for methanol from renewable wood biomass is  $-0.914$  kg CO<sub>2</sub>eq/kg methanol, and the corresponding energy use is 17.7 MJ/kg methanol. The inventory results for this case are shown in Table 2F.

**Table 2F.** LCI results for methanol from wood biomass (Case F).

	Unit	Value	Reference & Notes
Input gasification, WGS and methanol production			Andersson et al. [24]
Wood	kg/kg CH <sub>3</sub> OH	3.112	
Electricity	MJ/kg CH <sub>3</sub> OH	4.787	
Oxygen	kg/kg CH <sub>3</sub> OH	1.521	
Output			
Net district heat	MJ/kg CH <sub>3</sub> OH	6.421	
Methanol (CH <sub>3</sub> OH)	kg	1	
Ash	kg/kg CH <sub>3</sub> OH	0.047	
Primary pollutants gasification, WGS and methanol production			
GWP <sub>100</sub> for biomass harvesting and transport	kg CO <sub>2</sub> eq	0.1535	Melin et al. [20]
GWP <sub>100</sub> for power consumption	kg CO <sub>2</sub> eq	0.0612	Moro and Lonza [38]
CO <sub>2</sub>	kg/kg CH <sub>3</sub> OH	-1.129	negative value
GWP <sub>100</sub> for methanol production from wood biomass	kg CO <sub>2</sub> eq	-0.9143	negative value
Energy use (55.3% efficiency on LHV)	MJ/kg CH <sub>3</sub> OH	17.647	
Reference value			
GWP <sub>100</sub> for methanol production from coal	kg CO <sub>2</sub> eq	2.6–3.8	Matzen et al. [35]

The negative GWP<sub>100</sub> for methanol production derives from the use of renewable wood biomass and is better than that of power production from 50:50 co-gasification of coal and biomass (Alternative 1F in Figure 6, Trop et al. [21]). Part of the impact is due to the very low electricity emissions in Sweden.

Biomass drying has a significant impact on the overall energy balance. The gasification unit produces excess heat, increasing the cooling demand by 60% when drying of the biomass is not integrated with the process. Oxygen gasification produces an exit gas with a heating value of 10–14 MJ/Nm<sup>3</sup> [22]. A humidity increase from 40% to 50% of the wood feedstock reduces the biomass-to-methanol overall efficiency from 55% to 50% [23]. An alternative for Case F is methanol production from biomass/black liquor integrated with a PPM. According to [24], integration of methanol production with a PPM improves the system efficiency by 7%.

The methanol yield can be increased by adding hydrogen to the syngas prior to methanol synthesis. The impact on the GWP<sub>100</sub> depends on how the H<sub>2</sub> is produced. The source of electricity is vital; power produced in a condensing coal power plant emits 925 kg CO<sub>2</sub>eq/MWh and 419 kg CO<sub>2</sub>eq/MWh in an NG combined cycle plant [23]. Using electricity produced from natural gas would, in Case F, change the electricity emissions to 116.39 g CO<sub>2</sub>eq/MJ from the 12.78 g CO<sub>2</sub>eq/MJ used for base case F in Table 2F. Correspondingly, the GWP<sub>100</sub> for methanol production from wood biomass would change from  $-0.914$  to  $-0.418$  kg CO<sub>2</sub>eq/kg methanol (Alternative 2F in Figure 6).

### 3.2. Greenhouse gas emissions and energy use

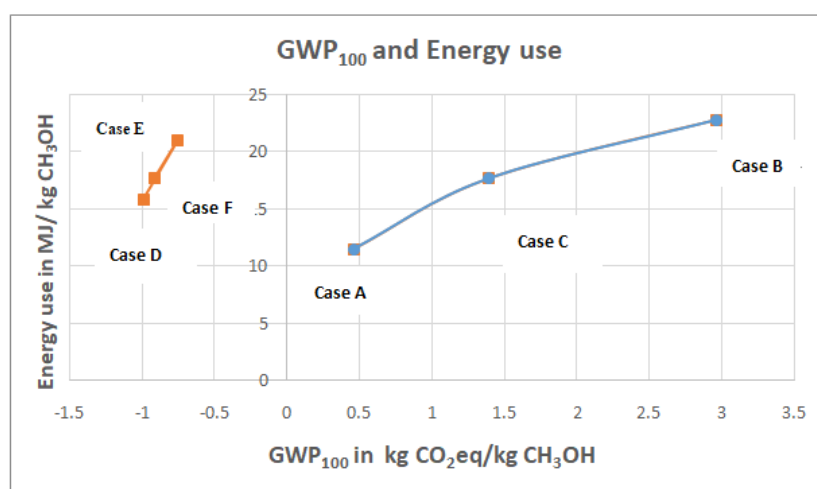
This study covers two impact categories: Namely GWP<sub>100</sub> and energy use. The overall results for GWP<sub>100</sub> and energy use are presented in Table 3. The results are based on the LCI data shown in Section 3.1, and on the overall efficiency based on LHV percentages varying from case to case. If the overall efficiency gives a higher energy use than the LCI data in Section 3.1, the higher value is selected for Table 3. The highest efficiency of 66% is for the methanol from NG (Case A), and the lowest efficiency of 51% is for the methanol from fossil CO<sub>2</sub> and H<sub>2</sub> from electrolysis (Case E). The GWP<sub>100</sub> values show a greater variation. The highest GWP<sub>100</sub> value of 2.965 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH is for the methanol from coal (Case B), and the lowest negative value of -0.989 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH is for the methanol in co-production with renewable corn ethanol (Case D). Example calculations of energy use are in the Supplementary material. Overall efficiencies are from respective references.

The tri-reforming process (Case C) utilizes practically an equal amount of CH<sub>4</sub> as Case A for methanol production, and cannot therefore be considered fully resource-efficient. The only benefit is the captured CO<sub>2</sub> from the coal-fired power station. The correlation between GWP<sub>100</sub> and energy use is almost linear, both for positive and negative GWP<sub>100</sub> impacts (Figure 3). The impact of the economic allocation of primary feedstock emissions in the co-production of methanol and corn ethanol (Case D) provides a benefit in terms of reduced biomass harvesting, processing and transport emissions compared to stand-alone production of methanol from wood biomass (Case F).

**Table 3.** GWP<sub>100</sub>, overall efficiency and energy use for the six assessed cases of methanol production.

	Case A	Case B	Case C	Case D	Case E	Case F
GWP <sub>100</sub> in kg CO <sub>2</sub> eq/kg CH <sub>3</sub> OH	0.462	2.965	1.392	-0.989	-0.752	-0.914
Overall efficiency on LHV basis in %	66	57.7*	56	58	51	55.3
Energy use in MJ/kg CH <sub>3</sub> OH**	11.446	22.786	17.731	15.809	20.976	17.647

\*Cold gas efficiency of methanol synthesis on HHV basis instead of overall efficiency on LHV basis. \*\*Including unreacted feedstock.



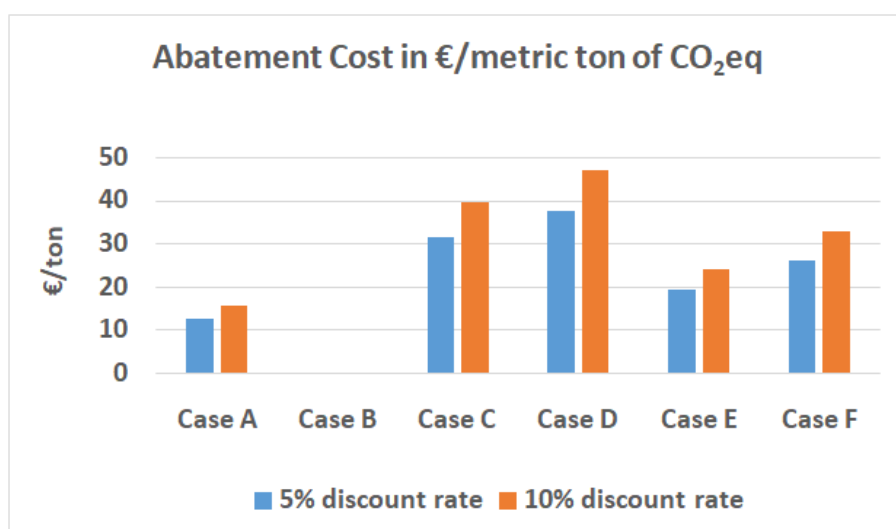
**Figure 3.** GWP<sub>100</sub> and energy use for the six assessed cases of methanol production.

The difference between similar technologies (Cases D and E) is less than one would anticipate between biogenic and fossil CO<sub>2</sub>. The absolute difference in the GWP<sub>100</sub> impact between Case D and Case E is 0.237 kg CO<sub>2</sub>eq/kg CH<sub>3</sub>OH. 50.2% of this can be attributed to the efficiency difference with the rest originating from the different allocation methods (economic and energy) and the benefits of biogenic CO<sub>2</sub>.

### 3.3. Carbon dioxide equivalent abatement cost and methanol production cost

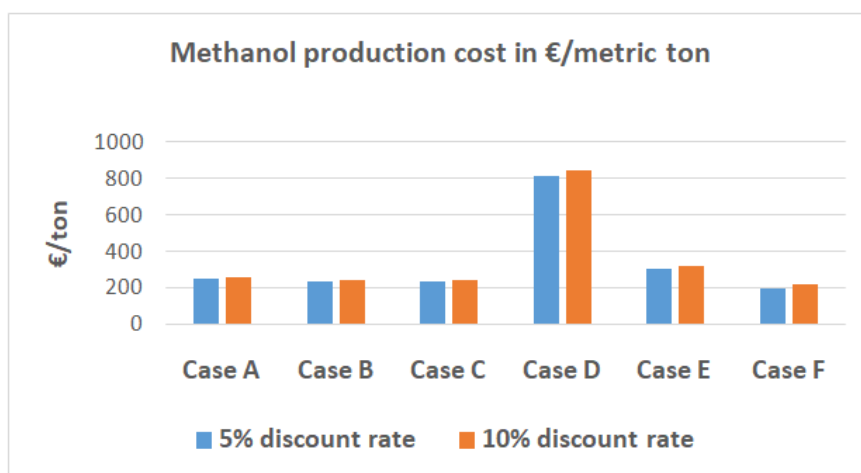
A preliminary CO<sub>2</sub>eq abatement cost estimation for cases A, B, C, D, E and F was performed using the CRF, as defined in Section 2. The investment and operational cost data, the annual production capacity of methanol and avoided amount of CO<sub>2</sub>eq compared to the reference value are shown in Table 4. The reference value for all cases is 2.6 kg CO<sub>2</sub>eq/kg methanol (i.e. the coal-based process) [35]. The methanol from gasification of coal (Case B) does not generate avoided emissions. The CO<sub>2</sub> abatement cost is shown in Figure 4, and the production cost of methanol in Figure 5.

The two discount rates indicate the sensitivity of abatement and production cost for changes in the investment cost and profitability rate required. The production cost of methanol with a 5% discount rate varied between €197 and €305 per metric ton of methanol for most of the cases. The only exception is methanol in co-production with corn ethanol (Case D) with €810 per metric ton of methanol.



**Figure 4.** Abatement cost for avoided emissions.

This is explained by the high operational cost combined with a small production capacity. Correspondingly, with a 10% discount rate, the variation was from €220 to €321 per metric ton of methanol, and accordingly Case D achieved €844 per metric ton of methanol. The lowest production cost is for methanol produced from wood biomass inside a PPM. At current methanol prices of US\$500 per metric ton of methanol, all cases with the exception of case D can be considered viable options. The example calculations of discounted abatement cost and discounted production cost of methanol are given in the Supplementary material.



**Figure 5.** Methanol production cost in € per metric ton of methanol.

### 3.4. Sensitivity and limitations of results

The results are impacted by the robustness of the assumptions made, the quality of the obtained data, and the limitations arising from the methodology used. The ALCA method used in this evaluation reflects the production systems as they are described in their respective references. In a sense, this is a clear limitation, and bounds the results to the technologies, efficiency and allocation factors, feedstock resources, and geographical locations used in the assessment.

The uncertainty of results attributable to different efficiencies and initial process data for LCI tables are partly normalized using one energy value for methanol in all cases to extract the  $GWP_{100}$  impact. This gives a variation between 1.7% and 12.8%, and reflects the uncertainty of results. The energy use for Case D and E was estimated using efficiency values.

Alternative cases for  $GWP_{100}$  impact are listed in Table 5 and the sensitivity of results is illustrated in Figure 6. The reference value for all the cases is methanol production from coal with a  $GWP_{100}$  of 2.6 kg  $CO_2eq/kg$   $CH_3OH$ .

**Table 4.** Input data for  $CO_2eq$  abatement cost and methanol production cost calculations.

	Case A	Case B	Case C	Case D	Case E	Case F
Methanol production capacity in 1000 metric tons/year	2000	864	1419	32	1668	259
$GWP_{100}$ impact in kg $CO_2eq/kg$ methanol	0.462	2.965	1.392	-0.989	-0.752	-0.914
Reference value in kg $CO_2eq/kg$ methanol	2.6	2.6	2.6	2.6	2.6	2.6
Avoided $CO_2eq$ amount in 1000 metric tons/year	4276	0	1714	116	5590	910
Investment cost reference	Zhang et al. [40]	Trop et al. [21]	Zhang et al. [40]	Matzen et al. [35]	Räuchle et al. [1]	Andersson et al. [24]
Total investment cost in M€	828	632.2	835	33.62	2080	369

*Continued on next page*

	Case A	Case B	Case C	Case D	Case E	Case F
Service life of investment in years	20	30	20	10	30	20
Annual operational hours	8000	8400	8400	8000	8000	8400
Annual operational cost in M€	444	170	282	21.83*	400*	27
Investment to cover first 10 years of operation in M€	414	253	417	33.62	832	184.5

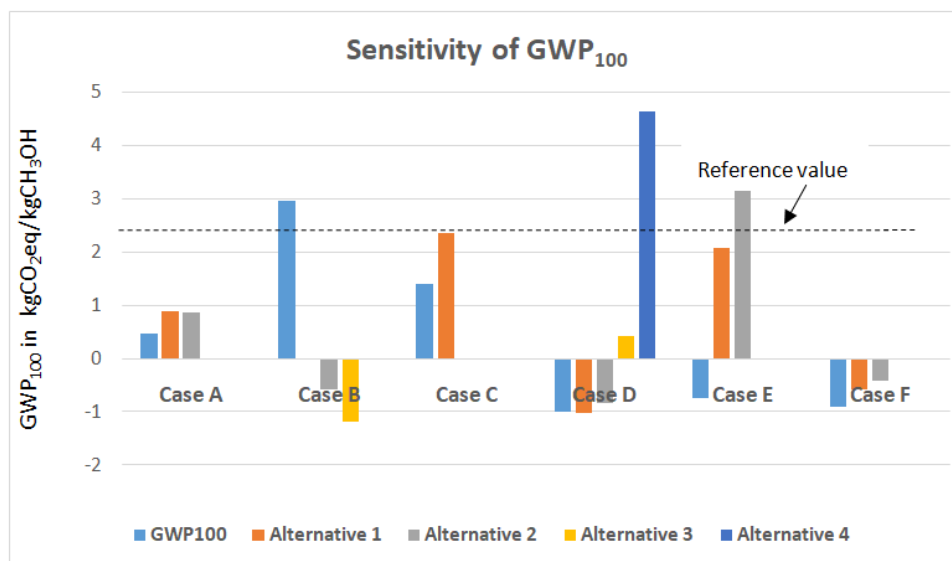
\*Note: Operational costs normalized to €40/MWh wind energy for H<sub>2</sub> production from €67/MWh for Case D and from €20/MWh for Case E.

**Table 5.** Alternatives used for the assessment of sensitivity in kg CO<sub>2</sub>eq/kg methanol.

	Case A	Case B	Case C	Case D	Case E	Case F
Base Case	Methanol from Norwegian NG	Methanol from coal gasification	Methanol by tri-reforming integrated with power production	Methanol in co-production with corn ethanol and DSG	Methanol from captured CO <sub>2</sub> and H <sub>2</sub> from electrolysis	Methanol from wood biomass
Base Case GWP <sub>100</sub>	0.462	2.965	1.392	-0.989	-0.752	-0.914
Alternative 1	0.881, NG from Algeria upper limit*	0, 40% biomass in gasification**	2.353, power emissions included	-1.008, only CO <sub>2</sub> , CH <sub>4</sub> and N <sub>2</sub> O included	2.068, H <sub>2</sub> produced in petroleum refinery	-0.590, with 50/50 coal/biomass feed
Alternative 2	0.873, NG from Algeria lower limit*	-0.590, 50% biomass in gasification		-0.83, all H <sub>2</sub> emissions included	3.181, H <sub>2</sub> with grid power in Germany	-0.418 electricity from NG
Alternative 3		-1.18, 100% biomass in gasification		0.418 H <sub>2</sub> from NG		
Alternative 4				4.642 H <sub>2</sub> from coal		

\*Reference values from Trudewind et al. [28], \*\*Reference value from Meerman et al. [17].





**Figure 6.** Sensitivity of GPW<sub>100</sub> impact assessment in kg CO<sub>2</sub>eq/kg methanol.

#### 4. Discussion

The evaluation of optimal system solutions requires, in addition to environmental and energy efficiency issues such as GWP<sub>100</sub> impact and energy use, an economic evaluation of the technologies. Instead, we have included a preliminary estimate of the CO<sub>2</sub>eq abatement cost for the GWP<sub>100</sub> reduction compared to a reference case of methanol production from coal. In addition, we evaluated the preliminary production cost of methanol for each case. The GHG emissions connected to land use change are not considered in this study. We selected attributional LCA in combination with GHG abatement and methanol production cost evaluation as an assessment tool. Many other tools exist, and one of the more complex methods is a 3-dimensional assessment including LCA, life cycle costing (LCC) and social life cycle assessment (S-LCA) [41]

The results of this study implicate the importance of comparing different solutions in a uniform manner. Especially, the case of tri-reforming (Case C: Producing energy by steam reforming, using the flue gas together with natural gas for methanol production) illustrates that there is a trade-off between the positive GWP<sub>100</sub> impact and overall resource efficiency (Table 2C). It can be argued that the energy or economic allocation of both resource and energy use, in this case, between net electricity, district heat and methanol gives overall benefits. Therefore, when assessing co-production facilities, it is vital to remember that overall feasibility depends on the allocation of environmental and energy loads between different products and side streams.

Our results are comparable with previous research, although we have not identified similar research with an assessment of a wide range of technologies concentrating on GWP<sub>100</sub> and energy use. Compared with similar cases in China [2], where methanol production from methane has a conversion efficiency of 59% on an LHV basis, and that from coal 39% on an LHV basis, our results show lower GWP<sub>100</sub> and energy use due to the efficiency difference. The results for methanol from CO<sub>2</sub> and H<sub>2</sub> (Cases D and E) agreed well with the results of Van-Dal and Bouallou [42], who reported a negative emission of 1.15 kg CO<sub>2</sub>eq/kg methanol in the synthesis part without deducting emissions in CO<sub>2</sub> and H<sub>2</sub> production. The tri-reforming route (Case C) practically halved the GWP<sub>100</sub>

impact in comparison with Case B, and this is supported by the results of Zhang et al. [14] for methane-based tri-reforming with flue gas input, although the processes themselves are not comparable. The wood biomass route (Case F) with 55.3% overall efficiency is in line with the 53.9% reported by Van Rens et al. [18].

Thermodynamically feasible solutions might not always be environmentally optimal. Our results (Case D and E) are comparable with the findings of Dumont et al. [43] concluding (1) that GWP values for CO<sub>2</sub> exceeding 0.276 kg CO<sub>2</sub>eq/kg CO<sub>2</sub> make CH<sub>4</sub> a better option than CO<sub>2</sub> for methanol synthesis, and (2) the GWP for the H<sub>2</sub> used in the synthesis and values below 0.53 kg CO<sub>2</sub>eq/kg H<sub>2</sub> overrule any other carbon source than captured/recycled CO<sub>2</sub>. Environmentally feasible solutions are not always economically viable solutions, as demonstrated by our case of methanol in co-production with corn ethanol (Case D).

Transporting resource materials and intermediates between different geographic locations has a considerable impact on the overall GWP<sub>100</sub> performance (Case B). Especially, the leakage of methane, carbon dioxide and nitrous oxide are related to the transport distance. Similarly, the emissions of power generation easily change the positive impacts to unexpectedly high negative results, as in the case of hydrogen production (Case D). This study shows that results of the LCA are altered drastically by changing the raw material production route or other assumptions. The resource for H<sub>2</sub> production and GHG load of electricity in electrolysis are both factors impacting the GWP<sub>100</sub>.

Global climate change has no regional or local environmental boundaries. In the case of methanol production, CO<sub>2</sub> is the main contributor to the impact of GHG. Positive development is ongoing also in enhancing the current production route of methanol from NG. A recent modelling study showed a net potential for CO<sub>2</sub> emissions reduction of 0.36 ton CO<sub>2</sub>/ton methanol [44]. Producing methanol by gasification from wood biomass (Case F) can compete in positive GWP<sub>100</sub> impact with co-firing coal and biomass for electricity and district heat production (Alternative 1F). Yet, wood biomass or any other biomass has many competitive uses. The production of methanol from wood biomass would compete with the production of FT liquids, other chemicals and with the standard products of PPMs. The competition in raw materials makes the captured CO<sub>2</sub> routes more suitable for the production of methanol, provided that the production costs remain competitive. However, with limited fossil or renewable carbon resources, it is more feasible to produce chemicals than to use the same resource as fuel. Storing renewable energy resources in methanol produced from hydrogen and captured CO<sub>2</sub> closes the carbon loop, and facilitates the circular economy approach in the production of valuable bulk chemicals. Growing demand in methanol is mainly in Asia Pacific where constraints in biomass supply may restrict the viability of biomass based methanol production.

However, there are several reasons and barriers that slow down the implementation of low carbon methanol processes and circular economy approaches in the production of bulk chemicals. These include the relatively long cycle of introducing new technological processes, subsidizing of the fossil resource base, and normative and legislative restrictions in the introduction of new raw materials and processes.

## 5. Conclusions

The life cycle environmental performance of methanol, on a cradle-to-gate basis, for six different production routes has been assessed using an attributional LCA. The assessment is limited

to the impact categories of GWP<sub>100</sub> and energy use. The sensitivity of the obtained life cycle inventory results (LCI) is illustrated by adding alternatives to the original base cases.

The best performing in terms of production cost and GWP<sub>100</sub> is methanol production from wood biomass located inside a pulp and paper mill (Case F). Production routes that perform well environmentally are Cases D and E, producing methanol from biogenic or captured fossil carbon dioxide, and renewable hydrogen (wind electricity). The former has the lowest, negative GWP<sub>100</sub> emission of 0.989 kg CO<sub>2</sub>eq/kg methanol. The highest GWP<sub>100</sub> value of 2.965 kg CO<sub>2</sub>eq/kg methanol is generated in the coal gasification process. However, the best GWP<sub>100</sub> impact (Case D) changes drastically to the worst if the production of hydrogen is altered from renewable electricity to coal-generated. In this case, the GWP<sub>100</sub> would change from a negative value to a high positive value of 4.642 kg CO<sub>2</sub>eq/kg methanol (Alternative 4D). Results of the LCA are clearly altered by changing the raw material base from fossil to renewable, and are especially sensitive to the source of electricity in producing H<sub>2</sub> by electrolysis.

The abatement cost of CO<sub>2</sub>eq with a 5% discount rate varied from €12.54 to €37.52 per metric ton of CO<sub>2</sub>eq, depending on the technology and reference level of CO<sub>2</sub>eq emissions. Methanol produced from NG has the lowest abatement cost with the highest for methanol in co-production with corn ethanol. The relatively high abatement cost of the latter is explained by the small annual production capacity combined with the high cost of renewable hydrogen production.

The production cost of methanol with a 5% discount rate varied from €197 to €305 per metric ton of methanol for most of the cases. The only exception was methanol in co-production with corn ethanol (Case D) reaching €810 per metric ton of methanol. Again this is due to the high operational cost combined with a small production capacity. In five cases of the six studied the production cost remains well below the current methanol market price of 600 €/ton. Finding break-even points for optimal capacity and production costs was out of the scope for this project.

The results indicate the load that methanol carries in terms of global warming potential and energy use. Storing renewable energy resources in methanol produced from hydrogen and captured carbon dioxide closes the carbon loop, and facilitates the circular economy approach in the production of valuable bulk chemicals.

The limitations of the current study are related to the accuracy of the process performance data in the original references, and to the assumptions made in performing the LCI calculations.

For future studies, the results would be complemented by a detailed economic performance evaluation of the technologies, including the potential of circular economy approaches in producing methanol.

## Conflict of interest

All authors declare no conflicts of interest in this paper.

## References

1. Räuchle K, Plass L, Wernicke HJ, et al. (2016) Methanol for renewable energy storage and utilization. *Energ Technol* 4: 193–200.
2. Su LW, Li XR, Sun ZY (2013) Flow chart of methanol in China. *Renew Sust Energ Rev* 28: 541–550.

3. MCGroup (2018) Methanol: 2018 World Market Outlook and Forecast up to 2027. Available from: <https://mcgroup.co.uk/researches/methanol>.
4. IHS. Methanol, Marc Alvarado, February 2016. Available from: <http://www.methanol.org/wp-content/uploads/2016/07/Marc-Alvarado-Global-Methanol-February-2016-IMPCA-for-upload-to-website.pdf>.
5. Brynolf S, Fridell E, Andersson K (2014) Environmental assessment of marine fuels: Liquefied natural gas, liquefied biogas, methanol and bio-methanol. *J Clean Prod* 74: 86–95.
6. Pontzen F, Liebner W, Gronemann V, et al. (2011) CO<sub>2</sub>-based methanol and DME—Efficient technologies for industrial scale production. *Catal Today* 171: 242–250.
7. Bermúdez JM, Ferrera-Lorenzo N, Luque S, et al. (2013) New process for producing methanol from coke oven gas by means of CO<sub>2</sub> reforming. Comparison with conventional process. *Fuel Process Technol* 115: 215–221.
8. Sauniois M, Jackson RB, Bousquet P, et al. (2016) The growing role of methane in anthropogenic climate change. *Environ Res Lett* 11: 1–5.
9. Riaz A, Zahedi G, Klemes JJ (2013) A review of cleaner production methods for the manufacture of methanol. *J Clean Prod* 57: 19–37.
10. Anicic B, Trop P, Goricanec D (2014) Comparison between two methods of methanol production from carbon dioxide. *Energy* 77: 279–289.
11. Tidona B, Koppold C, Bansode A, et al. (2013) CO<sub>2</sub> hydrogenation to methanol at pressures up to 950 bar. *J Supercrit Fluid* 78: 70–77.
12. Narvaez A, Chadwick D, Kershenbaum L (2014) Small-medium scale polygeneration systems: Methanol and power production. *Appl Energy* 113: 1109–1117.
13. Soltanieh M, Azar KM, Saber M (2012) Development of a zero emission integrated system for co-production of electricity and methanol through renewable hydrogen and CO<sub>2</sub> capture. *Int J Greenhouse Gas Control* 7: 145–152.
14. Zhang Y, Cruz J, Zhang S, et al. (2013) Process simulation and optimization of methanol production coupled to tri-reforming process. *Int J Hydrogen Energ* 38: 13617–13630.
15. Minutillo M, Perna A (2010) A novel approach for treatment of CO<sub>2</sub> from fossil fired power plants. Part B: The energy suitability of integrated tri-reforming power plants (ITRPPs) for methanol production. *Int J Hydrogen Energ* 35: 7012–7020.
16. Matzen M, Demirel Y (2016) Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: Alternative fuels production and life-cycle assessment. *J Clean Prod* 139: 1068–1077.
17. Meerman JC, Ramírez A, Turkenburg WC, et al. (2011) Performance of simulated flexible integrated gasification polygeneration facilities. Part A: A technical-energetic assessment. *Renew Sust Energ Rev* 15: 2563–2587.
18. Van Rens G, Huisman G, De Lathouder H, et al. (2011) Performance and exergy analysis of biomass-to-fuel plants producing methanol, dimethylether or hydrogen. *Biomass Bioenerg* 35: S145–S154.
19. Melin K, Kohl T, Koskinen J, et al. (2015) Performance of biofuel process utilising separate lignin and carbohydrate processing. *Bioresource Technol* 192: 397–409.
20. Melin K, Kohl T, Koskinen J, et al. (2016) Enhanced biofuel processes utilizing separate lignin and carbohydrate processing of lignocellulose. *Biofuels* 7: 31–54.

21. Trop P, Anicic B, Goricanec D (2014) Production of methanol from a mixture of torrefied biomass and coal. *Energy* 77: 125–132.
22. Holmgren KM, Berntsson T, Andersson E, et al. (2012) System aspects of biomass gasification with methanol synthesis—process concepts and energy analysis. *Energy* 45: 817–828.
23. Holmgren KM, Andersson E, Berntsson T, et al. (2014) Gasification-based methanol production from biomass in industrial clusters: Characterisation of energy balances and greenhouse gas emissions. *Energy* 69: 622–637.
24. Andersson J, Lundgren J, Marklund M (2014) Methanol production via pressurized entrained flow biomass gasification—Techno-economic comparison of integrated vs. stand-alone production. *Biomass Bioenerg* 64: 256–268.
25. Ortiz FJG, Serrera A, Galera S, et al. (2013) Methanol synthesis from syngas obtained by supercritical water reforming of glycerol. *Fuel* 105: 739–751.
26. Bludowsky T, Agar DW (2009) Thermally integrated bio-syngas-production for biorefineries. *Chem Eng Res Des* 87: 1328–1339.
27. Boretti A (2013) Renewable hydrogen to recycle CO<sub>2</sub> to methanol. *Int J Hydrogen Energ* 38: 1806–1812.
28. Trudewind CA, Schreiber A, Haumann D (2014) Photocatalytic methanol and methane production using captured CO<sub>2</sub> from coal-fired power plants. Part I—a Life Cycle Assessment. *J Clean Prod* 70: 27–37.
29. Bai Z, Liu Q, Lei J, et al. (2015) A polygeneration system for the methanol production and the power generation with the solar-biomass thermal gasification. *Energ Convers Manage* 102: 190–201.
30. Bertau H, Offermanns H, Plass L, et al. (2014) Methanol: The Basic Chemical and Energy Feedstock of the Future. Heidelberg: Springer.
31. ISO (2006a) Environmental Management—Life Cycle Assessment—Principles and Framework. ISO 14040:2006. ISO/IEC.
32. ISO (2006b) Environmental Management—Life Cycle Assessment—Requirements and Guidelines. ISO 14044:2006. ISO/IEC.
33. Cherubini F, Jungmeier G (2010) LCA of a biorefinery concept producing bio-ethanol, bioenergy, and chemicals from switchgrass. *Int J Life Cycle Assess* 15: 53–66.
34. Kajaste R (2014) Chemicals from biomass—managing greenhouse gas emissions in biorefinery production chains—a review. *J Clean Prod* 75: 1–10.
35. Matzen M, Alhajji M, Demirel Y (2015) Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix. *Energy* 93: 343–353.
36. Minutillo A, Perna A (2009) A novel approach for treatment of CO<sub>2</sub> from fossil fired power plants, Part A: The integrated systems ITRPP. *Int J Hydrogen Energ* 34: 4014–4020.
37. Barkley ZR, Lauvaux T, Davis KJ, et al. (2017) Quantifying methane emissions from natural gas production in north-eastern Pennsylvania. *Atmos Chem Phys* 17: 13941–13966.
38. Moro A, Lonza L (2017) Electricity carbon intensity in European Member States: Impacts on GHG emissions of electric vehicles. *Transport Res D-Tr E* 64: 5–14.
39. Moretti C, Moro A, Edwards R, et al. (2017) Analysis of standard and innovative methods for allocating upstream and refinery GHG emissions to oil products. *Appl Energy* 206: 372–381.

40. Zhang C, Jun KW, Gao R, et al. (2017) Carbon dioxide utilization in a gas-to-methanol process combined with CO<sub>2</sub>/Steam-mixed reforming: Techno-economic analysis. *Fuel* 190: 303–311.
41. Di X, Liping L, Weifeng S, et al. (2017) Life cycle sustainability assessment of chemical processes: A vector based three-dimensional algorithm coupled with AHP. *Ind Eng Chem Res* 56: 11216–11227.
42. Van-Dal ÉS, Bouallou C (2013) Design and simulation of a methanol production plant from CO<sub>2</sub> hydrogenation. *J Clean Prod* 57: 38–45.
43. Dumont MN, von der Assen N, Sternberg A, et al. (2012) Assessing the environmental potential of carbon dioxide utilization: A graphical targeting approach. *Comput Aided Chem Eng* 31: 1407–1411.
44. Yu Y, Jing L, Weifeng S, et al. (2018) High-efficiency utilization of CO<sub>2</sub> in the methanol production by a novel parallel-series system combining steam and dry methane reforming. *Energy* 158: 820–829.



**AIMS Press**

© 2018 the Author(s), licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)