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Green methanol from hydrogen and carbon dioxide using geothermal energy and/or hydropower in Iceland or excess renewable electricity in Germany

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A B S T R A C T

The synthesis of green methanol from hydrogen and carbon dioxide can contribute to mitigation of greenhouse gasses. This methanol can be utilized as either a transport fuel or as an energy carrier for electricity storage. It is preferable to use inexpensive, reliable and renewable energy sources to provide the energy needed for the green methanol production. Iceland has a large potential for such renewable energy sources. If only geothermal CO_2 may be utilized the green methanol potential in Iceland is ~340 million L/y. When all the potentially available geothermal energy and hydropower is combined the potential becomes ~2150 million L/y.

Next the scope is broadened to the European mainland using Germany as a case since its government has set strict goals for renewable electricity production. For Germany the electricity oversupply in 2050 is predicted to be 24 TWh_e/y, leading to a methanol potential of ~2360 million L/y using CO_2 from fossil fuel power plants.

In Iceland the potential of 340 million L/y of methanol as a transport fuel would supply all of the M3 demand and 75% of the M85 demand. In Germany the electricity oversupply would provide all of the M3 demand, but only 4% of the M85 demand.

1. Introduction

Increasing levels of CO_2 in our atmosphere impacting on the Earth's global temperature call for a more sustainable energy production. The European Union (EU) has set ambitious goals for GHG (greenhouse gas) emissions reduction of 80–95% by 2050. This implies that the energy sector should get about two thirds of its energy from RES (renewable energy sources). In its turn this implies that electricity production should be almost emission-free, despite an expected growth in demand [1]. Electricity from wind turbines and solar PV are expected to fulfil an important role in this transition. As these sources are intermittent surpluses of electricity need to be stored or converted to other energy carriers. Currently, H_2 (hydrogen) and CH_4 (methane) are in the picture to fulfil the role of storable energy carriers. Electricity surplus can be used to produce H_2 from water via electrolysis, or further react H_2 with CO_2 obtained from the burning of fossil fuels to synthesize CH_4 (Power-to-Gas). Apart from applying a lot of RES for electricity production there is another way to mitigate GHG emissions and meet renewable energy directives: Power-to-fuel. For this purpose the Icelandic company CRI (Carbon Recycling International) produces methanol (CH_3OH; [2]). In contrast to hydrogen and methane that could also be used as fuel methanol is a liquid which may give it some advantages (*e.g.* it can be stored at ambient temperature and atmospheric pressure). Besides blending with gasoline in cars, an application that can be started with directly as methanol is compatible with the current fuel infrastructure, or using it as fuel in fuel cells, methanol can also be used as feedstock in the chemical industry.

Currently, about 99% of all the methanol produced (global demand in 2011–2012 76,000 million L/y [3]) comes from using fossil fuels as feedstock, of which natural gas accounts for about 85% and coal for about 15%. The reasons are the relatively high hydrogen content of natural gas, the low energy consumption during the production and the relatively low investments costs. However, methanol can be produced more sustainably by synthesizing it from H_2 obtained via electrolysis and CO_2 [4]. It is no coincidence that this renewable, innovative method of synthesizing methanol is

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applied in Iceland. This country has a large potential for producing inexpensive renewable energy (hydropower and geothermal energy). The geothermal power plants in Iceland emit CO_2 due to the degassing of volcanic magma. CO_2 from these plants can be stored easily and used for methanol synthesis. Due to the available renewable energy and CO_2, Iceland can potentially produce methanol on a large scale [5]. However, building new methanol plants in Iceland requires new geothermal wells for supplying the energy (thermal and electricity) as well as supplying the CO_2. But when not all of the released CO_2 from these (new) wells is captured and used for methanol production, this production process actually leads to an increase in greenhouse gasses.

All in all it is important to investigate both the potential for the production of green methanol and its mitigating implications using Iceland as a case. Therefore, this paper first describes the situation in Iceland. Afterwards the scope is broadened to the European mainland using Germany as case since its government has strict goals for implementation of RES in electricity production, and because CRI has announced in December 2014 that a facility will be built in Germany using captured CO_2 from a coal-fired power plant [6].

2. Methodology

This research is divided in four parts: the methanol production, the case of Iceland, the case of Germany, and methanol as a transport fuel. With relevant data from literature the H_2 and CO_2 numbers are calculated together with the energy requirements of the methanol production process. Iceland is used as case to research possible pathways for the production of green methanol (used resources, power supply, etc.) and their potential. Germany is studied for its electricity oversupply potential, as the German government plans to install a lot of renewable electricity capacity leading to an imbalance between supply and demand. The oversupply is calculated using the simulation tool PowerPlan [7,8]. With the oversupply the methanol potential for Germany can be determined. One of the uses for methanol is as transport fuel, so this potential is researched for both Iceland and Germany.

3. Results

3.1. Methanol synthesis

According to the patents of the Icelandic company CRI, they use the Lurgi methanol processes [4,9] with H_2 and CO_2 as feedstock (equation (1)). H_2 is produced by the electrolysis of water (equation (2)) and CO_2 is recovered from a geothermal power plant located in Svartsengi. These two streams are compressed to approximately 50 bars and heated to a temperature of around 498 K. After leaving the reactor vessel, a mixture of unreacted H_2/CO_2, methanol and water (by-product), flows through a heat exchanger to preheat the inlet gasses. Hereafter, this mixture flows to a preheater for the distillation system and then methanol is condensed in a condenser [10,11,12].

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H = -49 \text{kJ/mol} \quad \text{Reactor} \tag{1}$$

$$2H_2O \rightarrow 2H_2 + O_2 \quad \text{Electrolysis} \tag{2}$$

Next, the steps in the methanol production will be described in terms of energy, starting with the two raw materials H_2 and CO_2.

3.1.1. Hydrogen production

The required energy for the electrolysis process is generated by RES. The idea of using renewable energy for producing hydrogen is not new and it was already mentioned as an option in 1975 [13]. However, the interest in renewable hydrogen production only started in the 1990s, when people became concerned about climate change and the diminishing fossil fuel reserves. Currently, there are three types of electrolyzers for hydrogen production, namely alkaline, PEM (polymer electrolyte membrane) and SOEs (solid oxide electrolyzers). Alkaline is the most mature technique, suitable for large scale, but it needs a constant input of electricity, which poses a potential problem when the facility is directly coupled to an intermittent renewable electricity supply. PEM electrolyzers are in their demonstration stages and are capable of processing a fluctuating input, thereby making them the best option for small scale commercial hydrogen production. SOEs are still in the R&D stage and they are based on high temperature electrolysis [14]. It is not known which type or brand electrolyzer unit the Icelandic company CRI uses for its production of green methanol. However, in a project of Shell and the Icelandic government, they built the world's first commercial hydrogen facility (for transport purposes) with an electrolyzer from NEL [15]. In this research it is therefore assumed that CRI also uses the highly efficient electrolyzers from NEL (bipolar alkaline) in the new commercial methanol production facilities. Table 1 presents the specifications and energy consumptions of the NEL electrolyzer. Electrolyzer units only require raw water (at ambient temperature) and electricity as an input. The purification of raw water and the separation of oxygen, hydrogen and unreacted water are included in the energy requirements of an electrolyzer unit.

3.1.2. CO_2 recovery

CO_2 can be obtained from several sources such as from flue gas of existing NG (natural gas), coal-fired or IGCC (integrated gasification combined cycle) electricity power plants; from geothermal media (Iceland); or from atmospheric air. One should keep in mind is that CO_2 recovery from power plants reduces the overall efficiency of electricity generation. This is mainly because capturing

Table 1
Specifications and energy consumptions of the bipolar alkaline electrolyzer unit NEL Atmospheric Type No. 5040 (5150 Amp DC).

Capacity [kg/day]	Conversion efficiency[a]	Energy consumption [kWh/kgH_2][b]	Product pressure [bar][c]	Energy efficiency (incl. pressure)[d]	Energy consumption without compression [kWh/kgH_2][e]	Energy efficiency (excl. pressure)[f]
1046	80%	54	30	74%	52	76%

[a] *Conversion efficiency*: the efficiency of converting water into hydrogen and oxygen. Water that has not been used in the electrolysis process is recycled. A lower conversion efficiency means a higher energy consumption [16].

[b] *Energy consumption*: the overall energy consumption in kWh/kgH_2 that is reported by the manufacturer of the electrolyzer units.

[c] *Product pressure*: the hydrogen end pressure given in bars before it is stored. In an electrolyzer unit, compression of atmospheric hydrogen is in some cases included.

[d] *Energy efficiency (incl. pressure)*: the energy efficiency listed by the manufacturer. This includes compression of hydrogen.

[e] *Energy consumption without compression:* to fairly compare the energy consumption for hydrogen production, the end pressure is recalculated to atmospheric pressure because hydrogen compression is energy intensive. In this column, the energy consumption is given in kWh/kgH_2 at atmospheric pressure. For this justification, assumed is a polytrophic compression of hydrogen with an overall mechanical efficiency of 72%.

[f] *Energy efficiency (excl. pressure)*: the energy efficiency of hydrogen production with an atmospheric end pressure.

CO_2 is energy intensive [17]. This will then also affect the total energy requirement of green methanol production. The CO_2 concentrations (by volume) of each source are important to investigate the required energy for the recovery. Table 2 shows the CO_2 concentrations of the various sources.

For the NG or coal-fired power plants the best technique for CO_2 recovery is post-combustion recovery (i). For the IGCC power plants pre-combustion recovery can be installed, albeit being very expensive [17,23]. The third potential recovery technique, oxy-fuel combustion recovery, is still under development and is not yet applied in large scale power plants. After the combustion of fossil fuels, whether this is with a pre- or post-combustion system, CO_2 must be separated from other flue gasses. CO_2 from geothermal fluids must be separated mainly from H_2S [24]. The challenge of CO_2 recovery from atmospheric air is the relatively low CO_2 concentrations [21,25]. CO_2 can be recovered by passing a CO_2-containing medium through a solid or liquid absorber (this can be either MEA (monoethanolamine), MDEA (methyldiethanolamine), NaOH (sodium hydroxide) or MgO (magnesium oxide)). This absorber has to be capable of capturing only CO_2 and no other components in this CO_2-containing medium. Only a few PP (power plants) have an option for the recovery of CO_2. Based on published data on actual measurements of the required energy for CO_2 recovery, average energy consumptions are calculated. In Table 3, the relevant results are shown.

NG-fired PP have relatively clean flue gasses compared to coal-fired PP, which is better for CO_2 recovery from an energy point of view (PP Net efficiency for NG 48% vs. 22% for coal). This results in a weighted average recovery-related electric energy consumption of 1.69 MJ/kgCO_2. For coal-fired power plants it is slightly more with on average 1.77 MJ/kgCO_2. On the other hand, the recovery efficiency for coal-fired PP is slightly higher than for NG-fired PP. Geothermal steam in Iceland basically consists of water, CO_2 and H_2S. Other steam components are neglected in this research. According to Cleanindex [19] and Dunstall & Graeber [24], average geothermal steam contains about 0.4% CO_2 and 0.075% of H_2S (by volume). CO_2 and H_2S are both absorbed by MDEA and separated afterwards. The energy consumption of this process is around 1.16 MJ/kgCO_2 with a recovery efficiency of up to 90% [12,24].

3.1.3. Mass balance

A mass balance is constructed for the two reactions (equations (1) and (2)). To obtain 1 kg methanol (31.21 mol) 1.37 kg CO_2 and 1.13 kg H_2O are required. These values stem from the equations 1.37 kg CO_2 + 0.19 kg H_2 → 1 kg CH_3OH + 0.56 kg H_2O and 1.69 kg H_2O → 0.19 kg H_2 + 1.50 kg O_2.

The whole process can be divided in four main components: compression of gasses, reaction, distillation and auxiliary & losses.

Table 2
CO_2 concentrations by volume of various sources.

Source	CO_2 concentration by volume (%)	Reference
Flue gas Coal-fired/IGCC	12–15	[18]
Flue gas NG	3–10	[18]
Geothermal media (Iceland)	0.4–6	[19,20]
Atmospheric air	0.0384–0.0400	[21,22]

3.1.4. Compression of gasses

The compression of CO_2 and H_2 consist of two different steps: compression of fresh inlet gasses and compression of unreacted gasses from the reactor. The gasses have to be recycled multiple times to achieve a high conversion efficiency. In this research the recycle ratio 7.9 is used [37]. A polytrophic compression is assumed with an efficiency of 72%. The electrical Work (W) for the compression of gasses can be calculated using equation (3):

$$W = \left[\frac{n}{(n-1)}\right] * P_2 * V_1 * \left[\left(\frac{P_1}{P_2}\right)^{\frac{(n-1)}{n}} - 1\right] \quad (3)$$

where n is the specific heat ratio (C_p/C_v). For CO_2 $n = 1.289$ and for H_2 $n = 1.410$. The initial pressure for the fresh inlet gasses is set at 1 bar (100 kPa) and for the recycled gasses at 45 bar (4500 kPa). The end pressure is 50 bar (5000 kPa). The inlet volume with the specific temperature (V_1) for CO_2 is 0.547 m^3/kg and for H_2 $V_1 = 11.11\ m^3/kg$. Since hydrogen is the lightest element it has a large specific volume which results in a high energy consumption for compression. Although membranes are becoming available for electrochemical hydrogen compression [38], in this study the same manner of compression for both H_2 and CO_2 is assumed. In Fig. 1 the compression energy curves for CO_2 and H_2 are shown in MJ/kg. The compression energy needed for H_2 is ~25× higher than for CO_2.

3.1.5. Reaction

The reaction of carbon dioxide with hydrogen to form methanol (and water as by-product) is exothermic with the correct inlet temperature and pressure. The energy that is released can be calculated with equation (1). Heat that is involved with this is $\Delta H = -49.7$ kJ/molCH_3OH. This results in $-49.7 \times 31.21 = -1.55$ MJ/kgCH_3OH.

3.1.6. Distillation

In the distillation column raw CH_3OH and H_2O are separated. The inlet temperature of this mixture is ~333 K with a pressure of 1.5 bar. For separating both fluids methanol will be vaporised while water remains in a liquid phase. The total energy consumption of the distillation column, including losses, pumping and condensation of methanol, is estimated at around 1.96 MJ/kgCH_3OH. This is in line with conventional distillation columns in methanol production facilities with natural gas as a feedstock [39].

3.1.7. Auxiliary & losses

Based on specifications of four different power plants the average electrical energy consumption of all equipment and losses

Table 3
Summary of CO_2 recovery data for selected sources. The energy consumption depicted is the weighted average of the values found in the literature sources.

CO_2 source	Reference plant			Recovery plant			Absorber
	Energy consumption (MJ/kgCH_3OH)	PP capacity (MW_e)	PP Net efficiency	PP capacity (MW_e)	PP Net efficiency	Recovery efficiency	
Existing NG-fired PP	1.69	513	56%	429	48%	88%	MEA[a]
Existing Coal-fired PP	1.77	351	35%	275	22%	91%	MEA[b]
Geothermal steam	1.16	–	–	–	–	90%	MDEA[c]

[a] Refs. [26-30].
[b] Refs. [31-36].
[c] Refs. [12,24].

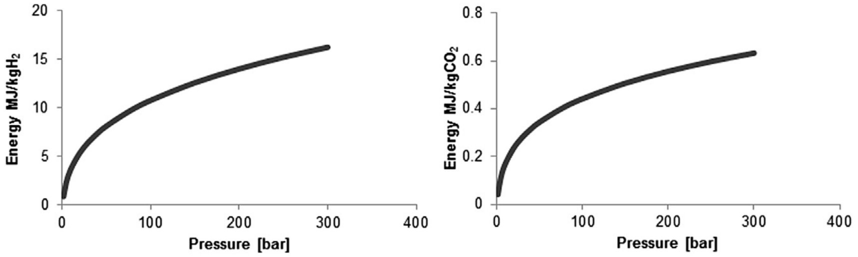

Fig. 1. Compression energy for H_2 (left) and CO_2 (right).

of a methanol factory are calculated. This leads to an electric energy consumption of 0.96 MJ/kgCH_3OH [40].

3.2. *Case study Iceland*

3.2.1. *Energy statistics*

In Iceland more than 85% of all primary energy consumption (~235 PJ) is generated by renewable energy sources (70% geothermal and 18% hydropower). As these sources produce relatively inexpensive electricity Iceland has the opportunity to cheaply supply its power-intensive industry (mainly aluminium production with a need of >12,000 GWh_e/y). Geothermal energy can be used for both electricity generation and heat purposes. In the primary energy use geothermal power is therefore the dominant source of energy, whereas in the case of electricity production hydropower is dominant (70% hydro vs 30% geothermal; [41]).

Currently, 52 hydropower plants are installed in Iceland (total capacity 1986 MW), which generated 12.9 TWh_e of electric power in 2013 [41,42]. Based on the total installed capacity and the electricity that is generated, an overall capacity factor can be calculated. For the year 2013 this was 0.74. This number is used to investigate the potential of new hydropower plants. According to Orkustofnun [43] 30 TWh_e/yr of hydropower can be utilized without damaging the environment too much while keeping it economically feasible (thermodynamic potential 187 TWh_e/yr).

Currently, 7 geothermal power plants are installed in Iceland with a total capacity of 663 MW_e. In 2013 these power plants generated a total amount of about 5245 GWh_e [41]. This results in an overall capacity factor of 0.90. Geothermal power has a lower future potential for electricity generation compared to that of hydropower. Estimated by Orkustofnun [43] is a potential of ~20 TWh_e/yr (capacity of ~2400 MW_e).

However, the calculations of Orkustofnun [43] are very rough estimations and only a few environmental and economic factors were taken into account. In contrast, the Icelandic government had a master plan developed to investigate the future of renewable electricity production in Iceland [44]. In this plan factors such as human impact on flora and fauna, vegetation, fishing in rivers, agriculture, geological formations, economic activity, employment and regional development were taken into account [44,45]. The master plan shows a maximum future capacity of ~1250 MW for hydropower and ~1400 MW for geothermal power. For hydropower this leads to a potential electricity production of 8050 GWh_e/yr and for geothermal power 11,000 GWh_e/yr (calculations based on Refs [41,42,45]). These potentials are used for scenario calculations.

3.2.2. *CO_2 emissions*

CO_2 emissions from geothermal power plants have always been seen as a drawback even when they emit significantly less CO_2 per generated kWh_e of electric power than fossil fuel power plants. Geothermal power plants use thermal energy derived from wells drilled to high depts. The plants in Iceland are located in volcanic areas that contain high amounts of CO_2 derived from metamorphism of carbonate rock. This means that CO_2 will be released into the atmosphere when it is not recovered by the power plant itself [46]. The emissions of the currently operating PP are shown in Table 4.

The latest data per plant are from 2010 where the total CO_2 emissions from geothermal power plants was about 186 kton. It can be seen that the old power plants emit the largest amounts of CO_2 per generated kWh_e (92–100 gCO_2/kWh_e). Orkuveriðvið Svartsengi is the site where CRI is located. According to Orkustofnun/NEA Iceland [47,48] this power plant emitted about 100 g CO_2/kWh in 2010. Newer power plants such as Hellisheiðarvirkjun & Nesjavallavirkjun from respectively 2006 and 1998 emit 5× less gCO_2 per kWh_e, even though they use thermal energy from almost the same geographical area. This phenomenon can partly be explained by the higher energy efficiency of these newer power plants [49]. In other words, less CO_2-containing steam is required for generation of the same amount of electric power. Furthermore, it is difficult to estimate the CO_2 concentrations from drilled wells due to natural fluctuations (see *e.g.* Ref. [20]). The CO_2 emissions of the new geothermal power plants described in Table 4 are ~20 gCO_2/kWh. These emissions are in line with the CO_2 survey study of Bertani and Thain [50]. The emissions of geothermal power plants account for 6% of the total anthropogenic CO_2 emitted in Iceland in 2010 [51]. Anthropogenic geothermal emissions in Iceland pale compared to the natural CO_2 emissions of geothermal activity [50,52,53]. For example the 2010 eruption of the volcano Eyjafjallajokull sent 2–3 times the annual anthropogenic Icelandic CO_2 amount in the air

Table 4
Current installed geothermal power plants with their specifications and CO_2 emissions. Calculations based on: Orkustofnun/National Energy Authority of Iceland [47,48].

Location	Power plant + opening year	Capacity [MW_e]	Electricity [GWh_e/yr]	CO_2 emissions [tons/yr]	[gCO_2/kWh]
Bjarnaflag	Aflstöð í Bjarnarflagi (1969)	32	256	962	**N/A**
Krafla	Kröfluvirkjun (1971)	60	480	44,515	**92.7**
Svartsengi	Orkuveriðvið Svartsengi (1977)	76.4	612	61,182	**100**
Reykjanes	Reykjanes á Suðurnesjum (1977)	0.5	4	N/A	**N/A**
Nesjavellir	Nesjavallavirkjun (1998)	120	961	20,201	**21.0**
Húsavík	OrkustöðHúsavík (2000)	2	16	N/A	**N/A**
Hellisheiði	Hellisheiðarvirkjun (2006)	213.4	1708	32,937	**19.3**

N/A = Data Not Available.

within 25 days [54,55]. The total Icelandic anthropogenic CO_2 emissions were 3405 kton in 2010, of which the industry accounts for 1589 kton, equaling 47% [51].

3.2.3. *Scenarios methanol production*

Five scenarios were developed for green methanol production in Iceland. For each scenario the following relevant subjects will be discussed:

1. Energy requirements of producing green methanol (MJ/$kgCH_3OH$)
2. Energy efficiency (Power-to-CH_3OH)
3. Maximum potential (L/yr)
4. Required electrolysers (#)
5. CO_2 input/output numbers

But first a short description of each scenario is given.

3.2.3.1. Scenario 1: CRI 5M. After having built a pilot methanol plant, CRI is currently using an industrial scale plant with a maximum capacity of 5 million liters of methanol a year. The required CO_2 will be captured with MDEA with a maximum of 90%. Hydrogen in this industrial scale plant is produced with a relatively low efficiency of 65%. The reason for this low efficiency is not known [10,12].

3.2.3.2. Scenario 2: Geothermal. In this scenario it is assumed that all potentially available geothermal power will be used to produce green methanol (11,000 GWh_e/y). The required CO_2 is recovered by the geothermal power plants with a maximum recovery efficiency of 90% (MDEA technique). The thermal energy required in the methanol production stems directly from geothermal sources.

3.2.3.3. Scenario 3: Hydro. In this scenario it is assumed that all potentially available hydropower will be used to produce green methanol (8050 GWh_e/y). Because no CO_2 source is available at hydropower plants, this has to be recovered by currently installed geothermal power plants with a maximum recovery efficiency of 90% (MDEA technique). The thermal energy required in the methanol production stems from electricity.

3.2.3.4. Scenario 4: Geothermal & Hydro. This scenario is basically a combination of scenario 2 & 3. The required CO_2 is recovered by the new and existing (when necessary) geothermal power plants with a maximum recovery efficiency of 90% (MDEA technique). Furthermore, hydrogen is produced in the same way as described in scenario 2 or 3 and the electrolyzer is located at each power plant to minimize transport losses.

3.2.3.5. Scenario 5: CO_2 as limit. When the required CO_2 should only be captured from renewable geothermal power plants, the availability of CO_2 becomes a limiting factor. The availability in existing geothermal power plants is calculated on the basis of current annual emissions. New geothermal power plants will emit less CO_2 per generated kWh_e. The totally available CO_2 from existing geothermal power plants is 168 kton when the recovery efficiency of 90% is taken into account. In potential new geothermal power plants this is 199 kton [47,48]. The rest of the scenario is equal to the geothermal scenario (Scenario 2).

In Table 5, a summary of each scenario is shown. The most energy-efficient scenario is the production of green methanol in combination with geothermal power (scenario 2). The individual energy requirements range between 42 and 48 MJ/$kgCH_3OH$. Therefore, the energy efficiency is between 47 and 54% (electricity-to-methanol).

The energy consumption includes all the steps in the methanol synthesis: H_2 production, H_2 compression, CO_2 recovery, CO_2 compression, distillation, and auxiliary/other. For all scenarios the production of H_2 accounts for more than 80% of the energy consumption. The compression of CO_2 costs the least energy (~2%), followed by auxiliary/other (~3%). The other components cost about the same amount of energy. The CO_2 input/output numbers consist of three entries. The maximum amount of CO_2 recovered is the amount per year needed to synthesize the methanol potential including the recovery efficiency. The production is the extra amount of CO_2 that will be emitted into the atmosphere due to the recovery efficiency. The total is the number of grams of CO_2 that is needed for the synthesis of 1 kg of methanol (including the recovery efficiency), but which in turn will be emitted into the atmosphere upon combustion of methanol.

The total maximum potential of Iceland (Scenario 4) is 2140 million liters of methanol a year. This is hardly 4% of the current worldwide methanol demand. To achieve this production, a minimum of more than 1000 large scale alkaline bipolar electrolyzers are required. This is technically possible but this type of electrolyzer has only been built once and the costs of purchase are extremely high. Also, the required CO_2 for this potential (2427 kton/yr) is significantly larger than is available from only geothermal power plants. Keep in mind that the total emissions from currently installed geothermal power plants is ‘just’ 168 kton/yr after correcting for the recovery factor. The geothermal capacity of electricity generation can be more than doubled, but the maximum available CO_2 for recovery is estimated at around 367 kton/yr. The rest of the required CO_2 should then come from another source like the aluminium industry (note that the energy requirements of CO_2 recovery from other sources than mentioned in this paper may be significantly higher than the recovery from geothermal fluids). Capturing CO_2 emissions from the industry (~1600 kton) would provide enough CO_2 for either the geothermal (~1450 kton) or hydro scenario (~975 kton). For the combined scenario (Scenario 4) the geothermal power plants plus the industry could provide 80% of the required CO_2. The total emissions of methanol production and the use of it are around 1400–1500 $gCO_2/kgCH_3OH$ depending on the recovery efficiency and the source of CO_2. The

Table 5
Summary of the five scenarios of green methanol production in Iceland for the alkaline bipolar electrolyzer of NEL.

	1: CRI 5M	2: Geo-thermal	3: Hydro	4: Geothermal + hydro	5: CO_2 as limit
Energy consumption (MJ/$kgCH_3OH$)	47.9	42.0	43.1	42.4	42.0
Energy efficiency (Power-Methanol)	47.4%	54.1%	50.3%	52.5%	54.1%
Potential (10^6 L/yr)	5	1275	865	2140	337
Required electrolyzers (#)	2	625	424	1049	165
Max. recovered CO_2 (kton/yr)	5.4	1448	979	2427	367
Total ($gCO_2/kgCH_3OH$)	1501	1395	1373	1386	1395
Production ($gCO_2/kgCH_3OH$)	127.6	21.4	0	12.4	21.4

combustion of methanol would generate approximately 1373 $gCO_2/kgCH_3OH$ (see mass balance).

3.3. Case study Germany

3.3.1. Energy statistics

In order for methanol to be produced sustainably RES are needed to provide the necessary electricity for the process(es). Germany is the country with the most ambitious goals with regard to the implementation of RES. In 2001 the German government implemented the Renewable Energy Act (Erneuerbare Energien-Gesetz (EEG)) to promote the development of RES. Amendments of the EEG in 2004 and 2009 established goals for RES shares in electricity production. After the disastrous events in the Fukushima nuclear reactor in 2011 the German government issued the 2012 EEG amendment in which nuclear energy power plants are to be phased out by 2022. This amendment also aims to increase the share of RES in the electricity generation to 80% by 2050 [56]. The proposed shares of the different energy sources by 2050 are depicted in Fig. 2.

The total electricity generated will be 599 TWh_e with a total installed capacity of 385 GW_e. In 2012 the total electricity generated was 580 TWh_e with a total installed capacity of 179 GW_e of which RES accounted for 22% of the electricity production [57]. In 2013 uranium and lignite were the largest electricity producers (together 44%). In the 2050 scenario these sources have disappeared. They have been replaced by solar energy (3× increase by 2050), wind onshore (3× increase by 2050) wind offshore (virtually non-existent in the mix of 2012 while 17% by 2050) and biomass (2× increase by 2050). As the share of RES increases providing storage becomes important due to the potential imbalance between supply and demand. The production of green methanol could be a solution to this imbalance problem. To determine the potential amount of methanol that could be produced first the oversupply in 2050 has to be calculated. Therefore, the scenario depicted in Fig. 2 is run in the simulation tool PowerPlan. The oversupply in 2050 is determined to be 24 TWh_e. This amount of energy is then used to calculate the methanol potential. Some assumptions were made in these calculations. A green methanol facility is located next to a potential CO_2 source, so possible transport losses of CO_2 and H_2 are neglected. The average energy consumption values and efficiencies of CO_2 recovery are used which were shown in Table 3. In Germany lignite-fired power plants account for a large part of the electricity generation; assumed is that these are comparable to existing (subcritical) coal-fired power plants. By 2050 lignite power plants are most likely phased out, while natural gas-fired PP and coal-fired PP will still provide a part of the electricity. Therefore, both are used in the calculations.

From Table 6 it can be seen that there is hardly any difference between different fossil CO_2 sources in methanol potential. The maximum methanol potential is ~2350 million L/y, whereby more than 1200 electrolyzers are needed and 2.6 Mton of CO_2 is utilized each year. As the annual CO_2 emissions of Germany are ~800 Mton/y this means that the greenhouse gas mitigating potential of green methanol is rather small.

3.4. Methanol as transport fuel

The best use for green methanol would be to use methanol as a transport fuel. In this section options for using methanol in passenger cars will be researched as replacement for conventional gasoline.

Green methanol can be used in a mixture with conventional gasoline to reduce the carbon footprint of the fuel. The first option is to use small amounts of methanol in a mixture in normal ICE gasoline passenger cars. Up to about 15% methanol can be added to conventional gasoline without adjustments to the engine. This type of fuel is called M15 and is used as a standard in the automotive industry (15% methanol and 85% conventional gasoline by volume; [58]). The second option is a mixture of 85% methanol and 15% gasoline (M85) which is another automotive standard. 100% use of methanol in IC engines is not recommended because of technical barriers such as cold-start problems and problems with the air/fuel ratio. Running on M85 requires small technical changes to new or

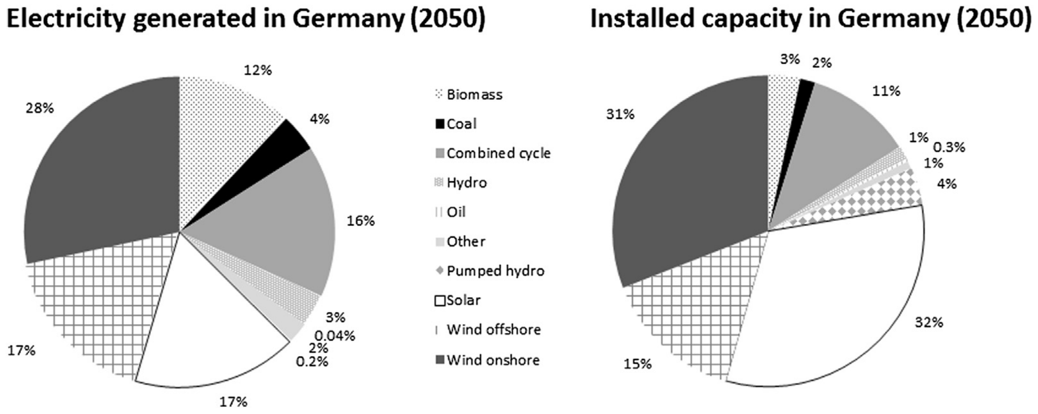

Fig. 2. Electricity generation and installed capacity for Germany in 2050.

Table 6
Results of green methanol production in Germany.

Potential oversupply (TWh_e/y)	CO_2 source	Energy consumption ($MJ/kgCH_3OH$)	Energy efficiency ($Power-CH_3OH$)	Potential (million L/y)	Recovered CO_2 (kton/y)	CO_2 emissions recovery ($gCO_2/kgCH_3OH$)	Total CO_2 input/output ($gCO_2/kgCH_3OH$)
24	Existing coal-fired	50.95	42.87%	2355	2560	64	1437
24	NG-fired	50.86	42.94%	2360	2565	22	1395

existing ICE vehicles (*e.g.* the installation of larger injectors and a methanol fuel tank). But these vehicles are then flexible and are able to run on a fuel with a methanol content between 0 and 85%, supplemented with conventional gasoline [58]. The current infrastructure can handle both M15 as M85, although small changes need to be made to fuel stations. Converting an existing fuel station into a methanol fuelling station would cost between $60,000 and $65,000. This is significantly lower than *e.g.* a new hydrogen fuel station with costs that are estimated at around $1 million per station [4]. However, methanol is more corrosive that conventional gasoline. In older passenger cars, especially cars with carburetors and lead-coated fuels tanks this could cause engine problems or even car accidents [59]. Due to a lower energy density of 19.7 MJ/kg compared to 47.2 MJ/kg for gasoline, a large(r) fuel tank has to be installed to compete with current standard vehicle ranges of up to 800 km. Furthermore, the automotive industry is currently more interested in ethanol (E85) rather than methanol (M85) because different limitations are set by the European Union (EU) for their blending percentages to achieve lower CO_2 emissions. In directive 2009/30/EC of the European parliament, a limitation of 3% by volume is set for blending methanol with conventional gasoline. For ethanol, this is higher with 10% by volume because blending ethanol is less toxic and hazardous than methanol [60].

Methanol can also be used directly in a proton exchange-based fuel cell for generating electricity to use in an electric car. In this direct-methanol fuel cell (DMFC), methanol is reformed into electricity, water, heat and CO_2. The working temperature of this DMFC is between 323 and 393 K, which is equal to a PEM fuel cell with hydrogen as fuel. The largest limitation of this type of fuel cell is the capacity, which is currently not larger than 5 kW_e. This means that DMFCs are not suitable for vehicle purposes, where a minimum capacity of 80 kW_e is required [4,61,62]. An alternative could be a reformed methanol fuel cell (RMFC), which has a larger capacity and can therefore function as a replacement for the internal combustion engine in our current passenger cars. In RMFCs, first hydrogen is generated from methanol. Subsequently the generated hydrogen is converted into electricity, water and heat. The conversion of methanol to hydrogen is relatively energy-efficient (70%). However, high temperatures are required (523–623 K), which is the main drawback when these cells are used in passenger vehicles [4,63]. The fuel cell efficiency is estimated at 39% in combination with on-board methanol reforming. Combining this with a drive-chain efficiency of 95% results in an overall energy efficiency of 26% (methanol-to-wheel). A battery electric car has an energy-efficiency (electricity-to-wheel) of ~90% and an ICE car (gasoline-to-wheel) 15–20% [64,65].

3.4.1. *Methanol demand/supply scenarios for transport*

In this section the different options for methanol in transport are examined for Iceland and Germany. As stated above, it is not allowed to blend more than 3% methanol by volume with gasoline within the European Union [60]. Therefore, M15 will not be calculated. According to the EU, M85 with 85% methanol and 15% gasoline is not a blending product of gasoline but is seen as a new type of fuel which is allowed within Europe. Therefore, only the demand for M85 and M3 (3% methanol and 97% gasoline) are discussed. RMFCs are also discussed to investigate whether these are a viable future option. Hereto all passenger cars (gasoline and diesel) will run on methanol in RMFCs.

In Germany there were 43.4 million passenger cars by the end of 2012 [66]. The fuel consumption of 46 billion liters of which 30.5 billion liters of gasoline (66%) and 15.5 billion liters of diesel (34%) was calculated by extrapolating the data of 2008 [67]. In Iceland, the number of cars is significantly lower with 210,000 at the end of 2012 [68]. The fuel consumption for automotive purposes was 294 kton of oil equivalent. Unfortunately, no information is known about the specific fuel consumption use of diesel or gasoline cars [68]. Assuming the same share of gasoline passenger cars compared to Germany results in a total gasoline demand of 240 million liters a year (and 122 million liter diesel). In the following methanol demand scenarios it is assumed that the fuel consumption of passenger cars in both Iceland and Germany will remain constant as well as the number of passenger cars.

In Table 7, the demand and supply results of the scenarios are shown. The demand in Iceland is combined with the five potential supply scenarios that were described in the section *Scenarios methanol production* (Scenario 1–5), which are shown in light grey. For Germany, the potential is discussed together with two scenarios where Iceland exports the produced methanol since the domestic market for methanol is rather small. For the export scenarios potential losses due to transportation from Iceland to Germany are neglected in this research.

About one third of the gasoline passenger cars in Iceland can potentially run on M3 with the current CRI facility. When CO_2 is not the limiting factor the potential in Iceland is large enough to fully supply the demand in M85 or the demand in methanol for RMFC

Table 7
Annual supply and demand of methanol in the transport sector.

Demand Scenarios → **Supply Scenarios** ↓		Potential (million liters)	M85	M3	RMFC
Iceland	Demand (million liters)		444	16	362
Germany			56508	1994	45982
Iceland (% of potential)	1: CRI 5M	5	1%	32%	1%
	2: Geothermal	1275	100%	100%	100%
	3: Hydro	865	100%	100%	100%
	4: Geothermal & Hydro	2140	100%	100%	100%
	5: CO_2 as a limit	337	76%	100%	93%
Germany (% of potential)	Green Revolution	2355	4%	100%	5%
	4: Geothermal & Hydro	2140	4%	100%	5%
	5: CO_2 as a limit	337	0.6%	17%	0.7%

passenger cars. When only the maximum available CO_2 from geothermal sources (~340 million L/y) is utilized three quarters of the demand in M85 can be supplied as well as almost all of the demand of RMFC passenger cars. In the case of Germany the projected oversupply can supply 100% of the M3 demand, but only 4% of the M85 demand. CRI wants to build more commercial green methanol factories to export their methanol to other European countries. In the best case situation, when Iceland will produce about 2150 million liters of methanol a year, it can only supply up to 5% of the demand for Germany when all the passenger cars are RMFC cars. For M3 this amount would be enough to supply all passenger cars. When CO_2 is the limiting factor the potential in export becomes too low to be profitable, even for M3.

4. Discussion

This study aimed to present an assessment of the potential of green methanol as a transport fuel and/or an energy buffer. The uncertainties in numbers in this paper are assumed to be in the range of 0–10%. Various uncertainties are associated with the calculations due to variances in the consulted literature. First of all, CRI is a small company that gives little information about its methanol production process. By using the most recent patents of CRI, it was assumed that they are using the Lurgi system based on a CuO/ZnO catalyst. However, on 1 June 2012, a news article appeared on the website of CRI. Therein it was claimed that the energy-efficiency was around 58% (electricity-to-methanol). In this study however, it was calculated that with the Lurgi system a maximum energy-efficiency of 54.1% was feasible, which was used in the calculations. It may be that CRI adjusted the Lurgi system. Secondly, much information is available about the potential of the Icelandic renewable energy sources. In this research data from the Icelandic government is used which developed a future master plan for implementing new geothermal and hydropower plants. The total potential of geothermal power was estimated at around 11 TWh_e/yr and for hydropower 8.2 TWh_e/yr. However, in some literature sources the total (technical) potential is estimated to be much larger with at least 20 TWh_e/yr for geothermal and 30 TWh_e/yr for hydropower. These values would lead to a larger methanol potential. Thirdly, CO_2 from geothermal power plants is used by CRI to produce green methanol. It is assumed that by building new geothermal power plants, the same amounts of CO_2 will be released as with existing geothermal power plants built after the year 2006. However, it is not well known what the actual available CO_2 from new geothermal power plants is and which amount can be used for methanol production. This could positively or negatively influence the estimated potential of Iceland. Fourthly, the potential in Germany is based on plans of the German government for the implementation of RES in the electricity production. These plans might change in the upcoming years if *e.g.* the economy changes. But Germany's largest utility E.ON has announced in November 2014 to exit the conventional energy market in favour of the renewable energy market [69]. This could make methanol not just a theoretical energy buffer and/or transport fuel, but a practical one.

But the largest barrier/challenge for methanol production is the method to produce the required hydrogen. In most literature, it is assumed that hydrogen easily can be produced by an oversupply of electricity. However, no electrolyzers exist yet that can handle an unpredictable and variable source of energy which will be generated from solar and wind power. Electrolyzer manufacturers will have to investigate the possibilities of combining solar and wind energy with the variable production of hydrogen. Furthermore, in the most extreme case presented in this study more than a thousand large scale bi-polar electrolyzers are needed to produce the required amounts of hydrogen. The feasibility of this will have to be examined as the company NEL has built such a large electrolyzer only once. If running on intermittent power sources is technically not possible or becomes energy inefficient, it is highly unlikely that green methanol factories will be built in countries that only have the possibility to implement solar PVs or wind power. In a study described by Gandía et al. [70], hydrogen is produced with an alkaline electrolyzer (bipolar) from the manufacturer Hydrogenics. Wind patterns from Sierra del Perdon (Spain) were used to simulate a realistic electricity output. The electrolyzer was able to produce H_2, but the efficiency decreased on average by 9% when using these patterns. An option to overcome this technical barrier might be to use Concentrated Solar Power (CSP) in high solar radiation areas. New CSP systems exist that can generate a constant and predictable output of electricity which can be used for the production of green methanol. Another issue of the electrolyzers is the limited theoretical efficiency of 83% at relatively low temperatures (293 K). However, the performance can be improved up to a theoretical efficiency of 92% by partly using thermal energy. This results in a lower electricity consumption during the production of hydrogen. In Iceland geothermal steam/water can be used as a heat source. In the case of Scenario 4 in Table 5 use of thermal energy would result in an increase in methanol potential of 60 million liter (to 2200 million L/y).

In this study, methanol is used in the transport sector as a replacement for conventional gasoline to indicate the potentials of Iceland and Germany. Using methanol in a passenger car is maybe not the best purpose from an energy point of view, but since the transport sector is one of the sectors that emits the most CO_2 it is necessary to review alternatives.

5. Conclusion

The synthesis of green methanol from H_2 (obtained via electrolysis) and CO_2 is possible on a large scale in Iceland. The limiting factor there is not the available amount of energy but the available amount of CO_2 when it is only captured from geothermal wells. With regard to the geothermal and hydropower potential the maximum possible methanol production is about 2150 million L/y, while the methanol potential drops to about 340 million L/y when only CO_2 from geothermal power plants can be utilized. This last potential is enough to provide M85 fuel for three quarters of the gasoline passenger cars and almost all of the demand in RMFC passenger cars in Iceland. For export purposes the potential of 340 million L/y is rather small, as only 1% of the German gasoline passenger cars could be fuelled with M85, and 17% when M3 is the fuel. Furthermore, as the current global demand for methanol is 76,000 million L/y a potential of 340 million L/y seems insignificant (<0.5%). If CRI is serious about the export of green methanol CO_2 needs to be captured from for example the Icelandic industry, but the costs and energy consumption of this are significantly higher than capturing CO_2 from geothermal PP. On top of that, the costs for green methanol production itself are already ~10× higher than for fossil methanol production from natural gas and ~5× higher than methanol from coal, mainly due to the expensive electrolysis process. Green methanol production can only compete with the fossil fuel-based production when the production will not be taxed or the production will be subsidized. Therefore, producing green methanol can only be achieved in countries which have the opportunity to use large amounts of inexpensive renewable energy sources, like Iceland.

The utilization of methanol as an energy buffer for surpluses of electricity production is possible. Methanol is currently a better option for an energy carrier than hydrogen and methane. Methane can be obtained from H_2 and CO_2 via the Sabatier process, but as this process requires 4 mol of H_2 to react with 1 mol of CO_2 instead of the 3 mol required for CH_3OH, and the production of H_2 requires by far the most energy in the overall process (80+%), methanol is a better option from an energy point of view. On top of that methanol can be implemented in the existing infrastructure, it can directly be used as a replacement for conventional gasoline and it can easily be transported and stored at ambient pressures and temperature. None is currently the case with hydrogen or methane as an energy carrier. For Germany the electricity oversupply was calculated and translated into a potential amount in green methanol of about 2350 million L/y. This is enough to provide all gasoline passenger cars with M3 fuel. But in the case of M85 or RMFC the potential supply will match just 4–5% of the demand. The recycled amount of CO_2 (2.6 Mton) this way (captured from NG- or coal-fired PP) is very small compared to the annual German CO_2 emissions of ~800 Mton.

Concluding, production of methanol from CO_2 and renewable H_2 represents a relevant means of storing energy and/or using it as a transport fuel, albeit being only applicable to countries where the demand is limited and large amounts of RES are available.

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