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Methane cracking as a bridge technology to the hydrogen economy

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ABSTRACT

Shifting the fossil fuel dominated energy system to a sustainable hydrogen economy could mitigate climate change through reduction of greenhouse gas emissions. Because it is estimated that fossil fuels will remain a significant part of our energy system until mid-century, bridge technologies which use fossil fuels in an environmentally cleaner way offer an opportunity to reduce the warming impact of continued fossil fuel utilization. Methane cracking is a potential bridge technology during the transition to a sustainable hydrogen economy since it produces hydrogen with zero emissions of carbon dioxide. However, methane feedstock obtained from natural gas releases fugitive emissions of methane, a potent greenhouse gas that may offset methane cracking benefits. In this work, a model exploring the impact of methane cracking implementation in a hydrogen economy is presented, and the impact on global emissions of carbon dioxide and methane is explored. The results indicate that the hydrogen economy has the potential to reduce global carbon dioxide equivalent emissions between 0 and 27%, when methane leakage from natural gas is relatively low, methane cracking is employed to produce hydrogen, and a hydrogen fuel cell is applied. This wide range is a result of differences between the scenarios and the CH_4 leakage rates used in the scenarios. On the other hand, when methane leakage from natural gas is relatively high, methane steam reforming is employed to produce hydrogen and an internal combustion engine is applied, the hydrogen economy leads to a net increase in global carbon dioxide equivalent emissions between 19 and 27%.

Introduction

Transformation of the global energy system is recognized as one of the most consequential factors to successful global warming mitigation, as the energy sector is responsible for about two-thirds of all anthropogenic greenhouse gas (GHG) emissions today [1]. Reduction of GHG emissions is a technological and societal challenge of vast dimensions, requiring a deep change of our energy system which is currently

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dominated by fossil fuels [2,3]. There is a general consensus about the need to shift from a fossil fuel-based to a sustainable, low-carbon society. According to the Intergovernmental Panel on Climate Change (IPCC), GHG emissions must be near or below zero by the end of the 21st century to limit warming to 2 °C relative to pre-industrial levels [4]. Such a transformation of our energy system will be a challenge, requiring new technological breakthroughs and renewable energy investments, and could take decades or generations to be carried out. In spite of the urgent need to reduce GHG emissions to limit the increase in warming, fossil fuels are expected to remain an overwhelming share of the worldwide energy demand at least until 2040 [2,3].

The hydrogen (H_2) economy has been proposed as a method for effecting this transformation, in which H_2 serves as one of the main global energy carriers [5]. H_2 can provide energy for transportation, buildings and industry, and can serve as a way to store energy [5]. Furthermore, it can be used as input to the H_2 fuel cell, which operates with a relatively high efficiency [5,6]. Importantly, the H_2 economy offers a way to mitigate global warming because H_2 oxidation is carbon-free. However, H_2 can be produced by a wide array of fossil fuel and sustainable energy sources, meaning that GHG emissions can be released depending on the type of production process [5,7–9]. Today, the majority of H_2 is derived from fossil fuels by steam reforming and gasification techniques [10,11]. Since these fossil fuel-based conventional technologies generate GHG emissions [10], they have the potential to offset H_2's environmental benefits. The low production costs of technologies utilizing fossil fuels compared to the relatively high costs of renewable alternatives suggests that this trend will not change in the foreseeable future [7].

In this context, the deployment of technologies that utilize fossil fuel resources while generating low or zero GHG emissions may be required in the meantime. These technologies may constitute a bridge between the current unsustainable energy system and a future sustainable society, as they satisfy world energy demand through available fossil fuel resources in an environmentally cleaner way during the development of a renewable-based system so as to keep GHG emissions under control.

Methane cracking may be considered a bridge technology. In this process, CH_4 is separated under high temperatures and in the absence of oxygen to produce elemental carbon and H_2, i.e., the reaction itself generates zero emissions of CO_2 [12–14]. Methane cracking has the potential to cross the bridge from our current carbon-intensive energy system, based on fossil fuels, to a low-carbon energy future. As fossil fuels will likely be required in the energy transition [14], a bridging solution is needed in which fossil fuels may be used with low or zero emissions to mitigate climate change until a sustainable system is developed. Another competing bridge technology is carbon capture and sequestration (CCS), which avoids CO_2 emissions to the atmosphere by storing CO_2 underground [15].

During the methane cracking process, unreacted CH_4 is separated from H_2, and is recirculated to the reactor. While the gas feedstock for methane cracking is mainly composed of CH_4, other hydrocarbons present are cracked in the same way as CH_4 by thermal splitting of the C–H bonds. In the absence of oxygen, H_2 produced by methane cracking is free of CO and CO_2, making methane cracking a suitable method to produce H_2 for fuel cells which require pure H_2. Another benefit of methane cracking is that the elemental carbon produced may possess an economic value because it is essential in the production of carbon fiber, which can be used in a variety of manufacturing applications. Nevertheless, developing a viable industrial implementation of the produced carbon for the economic benefits to be realized will be challenging [13,16].

Recent developments indicate that a large-scale, practical and viable application of this technology may be possible, by the process of bubbling methane into a liquid metal bath [17]. Lab-scale tests have overcome one of the main technological issues, i.e., carbon deposition leading to clogging of the reactor, which previously had prevented the development of methane cracking processes on the industrial-scale. For a practical and massive application of methane cracking, facilities to provide up to ~100–500 ton/day of hydrogen are required [18]. Work is in progress to advance the construction of a pilot plant to confirm the scalability of that technology.

The feedstock for methane cracking technology, natural gas, has been rapidly expanding in the United States due to significant advances in hydraulic fracturing and horizontal drilling in unconventional gas extraction [19,20]. While the upward trend of unconventional gas extraction has been mostly confined to the US, it is expected that this trend will continue globally [20]. Natural gas is often promoted as a bridging fuel on the road to a decarbonized energy system because it emits less CO_2 per unit of energy than oil or coal [21]. However, during the extraction, processing, and use of natural gas, CH_4 can escape to the atmosphere. This poses a problem to global warming mitigation because CH_4 is a potent GHG, with a global warming potential (GWP) of 86 over 20 years and 34 over 100 years [4], meaning that even small CH_4 leaks in the natural gas supply chain can have a large impact on global warming. The leakage rate of methane is thus critical in determining the overall climate impact of natural gas.

In 2011, Howarth and colleagues estimated CH_4 leakage rates for conventional natural gas production at 3.8% and unconventional at 5.8%, which factors in upstream (well site and gas processing) and downstream (transmission, storage, and distribution) emissions over the lifetime production of a well (i.e., full life cycle-based emissions estimate) [22]. These values were much higher than the United States Environmental Protection Agency's (US EPA) estimate for conventional gas at the time, which was 1.1% (no separate estimate existed then for unconventional natural gas) [23]. Since then, many reports have been published on CH_4 leakage estimates from natural gas production, giving a range of 0.47–6% for conventional and 0.67–7.9% for unconventional natural gas production over the lifetime production of a well [24]. Several top-down atmospheric measurement campaigns have also been performed which quantify CH_4 leakage rates from natural gas system activity at specific regions. CH_4 leakage rates published by these studies range from lower to significantly higher compared with EPA estimates, with values ranging from 0.18 to 17.3% [25–33].

In a review on 20 years of literature on CH_4 emissions from natural gas systems, Brandt et al. 2014 found that official inventories such as the US EPA frequently underestimate CH_4

emissions; nevertheless, he found that very high values found in some regional atmospheric studies are unlikely to be representative of typical emissions from natural gas systems. Therefore, considerable uncertainty still remains on the actual extent of CH_4 leakage from natural gas production. This is an important consideration when examining natural gas's viability as a bridging fuel, and in its promotion with technologies such as methane cracking to reduce the global warming impact. Other important considerations remain in addition to CH_4 leakage when promoting technologies that utilize natural gas, such as the potential impacts on water, environmental and air pollution, but these considerations are not addressed in this work, which does not have the aim of being a life cycle assessment (LCA) following the ISO 14040/14044 Standards and methodologies [34].

In this paper, a model for the evaluation of a hydrogen economy with the practical implementation of methane cracking is presented, and used to quantify the impacts on global emissions of CO_2 and CH_4. Scenarios are developed to illustrate the impact of replacing current industrial hydrogen production with methane cracking, and transport fuel with methane cracking-produced hydrogen, on emissions. The sensitivity of the results to CH_4 leakage rates from natural gas production is evaluated. Furthermore, other important parameters such as elemental carbon production from methane cracking, fugitive H_2 emissions, and the required efficiency of the methane cracking process are also analyzed.

Methods

Scenarios

Scenarios were designed to study different aspects of the methane cracking – hydrogen (MC-H_2) economy to evaluate the range of effects on global CO_2 and CH_4 emissions. The MC-H_2 economy is defined here as a H_2 economy facilitated by methane cracking. The scenarios were constructed as a projected snapshot of the present-day situation, in which the proposed changes are enacted immediately. Sectors of special interest to the MC-H_2 economy and therefore of focus in the scenarios are industrial H_2 production and road transportation. An overview of the scenarios is provided in Table 1.

Table 1 – Scenario overview.

Scenario	Full name	Description
Baseline	Baseline	Scenario representing actual situation and emissions regarding H_2 production and road transportation.
Industrial H_2	Industrial hydrogen	Methane cracking is fully implemented for production of industrial H_2.
RoadTrans H_2	Road transportation hydrogen	H_2 fuel is fully implemented to cover the energy needs of the road transportation sector. The H_2 implemented is produced by methane cracking.
Pessimistic RoadTrans H_2	Pessimistic road transportation hydrogen	H_2 fuel is fully implemented to cover the energy needs of the road transportation sector, in the context of pessimistic (high-emission) assumptions.
H_2Econ	Hydrogen economy	Contains implementations of both *Industrial H_2* and *RoadTrans H_2* combined in one scenario. This scenario is used to investigate various aspects of the H_2 economy, i.e., the upper limit of CH_4 leakage in natural gas production, and the methane cracking efficiency.

Baseline

A baseline scenario was developed to represent the present situation regarding industrial H_2 production and road transportation and their impact on emissions. This scenario was made as a means to compare alternative scenarios.

Industrial H_2

H_2 is a vital feedstock in the global chemical industry. Current values for global H_2 production are varied in the literature. For example, in the International Energy Agency's (IEA) 2007 report it estimates that 65 Mton H_2 are produced annually for industrial end-use applications [7], while Bond et al. 2011 estimate 47 Mton [35], and the US Department of Energy estimates >50 Mton [36]. In this work, the IEA value was assumed for industrial H_2 production since other data were also obtained from the IEA inventory (see Section Activity data).

Around 96% of global H_2 is derived from fossil fuels by conventional technologies, i.e., methane steam reforming, oil/naphtha reforming and coal gasification, which generate considerable GHG emissions (Table 2) [10]. Therefore, in the *Industrial hydrogen full penetration* scenario (*Industrial H_2*), methane cracking supplies current industrial H_2 demand, thereby replacing methane steam reforming, oil/naphtha reforming and coal gasification. Methane cracking does not replace electrolysis or the share of technologies producing H_2 for methanol synthesis (because the methanol reaction relies on syngas-H_2 and CO/CO_2, which is not produced by methane cracking).

CO_2 emission factors (EF) associated with H_2 production technologies are much greater in magnitude compared to those of CH_4, e.g., for coal gasification 107,000 kg CO_2 and 4 kg CH_4 are emitted per TJ (Table 2). This is because the CO_2 EFs are based on the carbon content of the fuel, and here reflect the assumption that 100% of the fuel's carbon gets oxidized during

Table 2 – Percent shares of global hydrogen production, and the corresponding emission factors (EF) for hydrogen production technologies [10,21].

H_2 production technology	Production share [%]		EF [kg/TJ][a]	
	Baseline	Industrial H_2	CO_2	CH_4
Methane steam reforming	48%	0%	54,500	2
Oil/naphtha reforming	30%	0%	71,100	4
Coal gasification	18%	0%	107,000	4
Electrolysis	4%	4%	0	0
Methane cracking	0%	96%	0	2

[a] These emission factors were calibrated [16] and selected from a range provided by the *IPCC 2006 Guidelines*.

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combustion. On the other hand, the CH_4 EFs represent fugitive emissions released from fuels, which are comparatively low in magnitude to CO_2 emissions in the energy sector [21].

RoadTrans H_2

The road transportation sector is responsible for generating a significant level of CO_2 and CH_4 emissions each year, primarily due to the use of oil and natural gas (Table 3). In fact, transportation accounts for nearly a quarter of global CO_2 emissions [37]. Therefore, in the *Road transportation hydrogen full penetration* scenario (*RoadTrans* H_2), oil and natural gas in road transportation are fully replaced with H_2 that is produced by methane cracking, while the relative shares of electricity and biofuels are kept the same. In this scenario it is assumed that vehicles are powered by hydrogen fuel cells, because fuel cells possess a relatively high tank-to-wheel efficiency (a measure of the drivetrain performance) compared to an internal combustion engine (ICE).

Pessimistic RoadTrans H_2

In the *Pessimistic road transportation hydrogen* scenario (*Pessimistic RoadTrans* H_2), H_2 fuel covers the energy needs of the road transportation sector as done in the *RoadTrans* H_2 scenario, but in the context of pessimistic assumptions. Specifically, it is assumed that H_2 fuel is produced by methane steam reforming, which is a conventional, fossil fuel-based (i.e., natural gas) H_2 production technology that releases CO_2 during the reaction process. Furthermore, it is assumed that CH_4 leakage rates from natural gas production are on the upper-end of the EF range, and that a H_2 internal combustion engine (ICE) is employed because this is considerably less efficient in terms of tank-to-wheel efficiency than H_2 fuel cell vehicles.

H_2*Econ*

The H_2*Econ* scenario is not handled like the previous scenarios, and instead is used for other applications of the MC-H_2 model discussed in Section Other aspects of interest to the MC-H_2 economy. The H_2*Econ* scenario contains the implementations assumed in the *Industrial* H_2 and *RoadTrans* H_2 scenarios.

Natural gas production methane leakage rates

The scenarios were calculated with three sets of CH_4 leakage rates in natural gas production, which cover a broad range of estimates in the literature that we consider reasonable. This was done to explore the impact of varying and potential CH_4 leakage rates in the natural gas system on total emissions in the scenarios. These sets were retrieved from EPA 1996 [23], Hultman 2011 [38] and Howarth 2011 [22] (see Table 4). The EPA 1996 values were used as lower-end rates, those from Howarth 2011 were used as higher-end rates, and those from Hultman 2011 were used as middle-value rates. However, for the *RT* H_2 *Pessimistic* scenario, upper-bound CH_4 leakage rates from Howarth 2011 were applied. Leakage rates are disaggregated into upstream and downstream processes from natural gas production. Upstream emissions occur at the well site and during gas processing, while downstream emissions occur during storage, transport and distribution of gas to customers. A distinction is made here between conventional and unconventional gas. Unconventional gas is obtained from relatively new sources that require unconventional methods for its extraction (e.g., hydraulic fracturing of shale gas), whereas conventional gas is obtained from traditional sources for which conventional methods can be used for its extraction. Aside from the extraction method, no difference is assumed between unconventional and conventional natural gas itself. Each calculation was performed twice, once assuming natural gas supply via 100% conventional natural gas, and once assuming natural gas supply via 100% unconventional natural gas. This was done to provide the full range of emissions estimates, because emissions are generally lower in conventional and higher in unconventional natural gas production.

Note that the downstream leakage rates displayed in Table 4 are representative of decentralized natural gas utilization. This is because these downstream leakage rates are higher than those that would result from centralized natural gas utilization. This is due to the fact that low-pressure urban distribution lines have a higher leakage rate than gas lines delivering natural gas to centralized power plants [20]. The decentralized downstream leakage rates were used to reduce complexity, so that the same rates could be employed for all segments of natural gas utilization in the model (i.e., for both industrial and private consumer end-use). While decentralized natural gas utilization leads to greater CH_4 emissions, decentralized production also has its own benefits with respect to methane cracking such as sharply reducing delivery

Table 3 – Road transportation energy share (based on energy activity per energy form for year 2012), and tank-to-wheel efficiency (TTW) in road transportation based on fuel type and energy converter [2,46].

Fuel type	Energy share [%]		Energy converter	TTW efficiency [%]
	Baseline	RoadTrans H_2		
Oil	92.8%	0%	ICE	22
Natural gas	3.8%	0%	ICE	16
Biofuels	2.4%	2.4%	ICE	22
Electricity	1.0%	1.0%	Battery	82
Hydrogen	0%	96.6%	Fuel cell	53
			ICE	28

Table 4 – Methane emission factor estimates expressed as a percentage of total natural gas produced.

Source	Upstream conventional gas	Upstream unconventional gas	Downstream
EPA 1996[a] [23]	0.2%	–	0.9%
Hultman 2011 [38]	1.3%	2.8%	0.9%
Howarth 2011 [22]	1.4%	3.3%	2.5%
Upper-end estimates of Howarth 2011 [22]	2.4%	4.3%	3.6%

[a] EPA 1996 [23] did not provide an EF for upstream unconventional gas. Therefore upstream unconventional gas is assumed to have the same EF as upstream conventional gas for EPA 1996 data.

and storage costs of H_2, and providing more independence to the consumer [39].

Displayed in Table 5 is an emissions comparison between natural gas, coal and oil, factoring in the three EF sets for natural gas provided in Table 4. The 20-year global warming potential (GWP) of CH_4 was used to convert CH_4 emissions into CO_2-eq emissions; the reason for this is explained in Section Emissions and CH_4 global warming potential. Note that the CO_2-eq for natural gas production is different among the EPA, Hultman and Howarth, since each of these sources have different CH_4 EF estimates.

Other aspects of interest to the MC-H_2 economy

Elemental carbon production from methane cracking

A side effect of methane cracking employed in the *Industrial H_2* and *RoadTrans H_2* scenarios is that elemental carbon (carbon black) is produced as a by-product of methane cracking. Today, carbon black production amounts to 8.1 Mton per year [40]. The carbon produced by methane cracking in the *Industrial H_2* and *RoadTrans H_2* scenarios was quantified at 170 and 790 Mton carbon per year, some orders of magnitude higher that the current black carbon market. The amount of high quality carbon produced by methane cracking will make this material available at a very low cost, likely boosting the development of new carbon-based technologies, for instance, graphene applications.

H_2 emissions

Incomplete combustion of fossil fuels and leakage of industrial H_2 are both sources of anthropogenic H_2 emissions. In the H_2 economy, H_2 emissions would be emitted during the production, transport, storage, and use of H_2. Increased H_2 emissions may exacerbate global warming by reducing the atmospheric concentration of the hydroxyl radical (OH), which would increase the lifetime of CH_4 and other trace gases [37,41]. For this reason, exploring the effects of increased H_2 usage on H_2 emissions is useful to understand ancillary effects of the H_2 economy on the climate. Therefore, H_2 emissions from H_2 fuel use in road transportation under the *RoadTrans H_2* scenario were quantified and compared to estimates on current H_2 emissions from incomplete combustion of oil and natural gas in road transportation by Wokaun and Wilhelm 2011 [42]. This provides the H_2 emissions balance that would occur in road transportation, i.e., the incurred H_2 emissions from introduced H_2 fuel use compared to the eliminated H_2 emissions from phased out oil and natural gas use. H_2 fuel leakage rates in road transportation of 1 and 2% were selected from Wokaun and Wilhelm 2011. While higher values of up to 4% were provided, these rates were deemed unrealistic as they would result in a huge commodity and significant monetary loss. Furthermore, it was found that industrial H_2 leakage rates from the H_2 distribution grid in Germany are already as low as 0.1% [41,43,44].

Table 5 – Aggregated emission factors for production of coal, oil and natural gas.

Fossil fuel production	EF [kg/TJ]		
	CO_2	CH_4	CO_2-eq
Coal[a]	–	450	39 000
Oil[b]	2900	280	27 000
Natural gas[c] (EPA 1996 [23])	4100	240	25 000
Natural gas[c] (Hultman 2011 [38])	4100	540	51 000
Natural gas[c] (Howarth 2011 [22])	4100	930	84 000

[a] Coal: The CO_2 EF is not provided in the literature because it is still being developed; therefore it is not included in this model. Note that the CO_2 EF for coal production is estimated to be low in comparison to the CH_4 EF. The CH_4 EF covers mining and post-mining emissions, averaged for underground and surface coal mines [21].

[b] Oil: The CO_2 EF covers oil production, transport and refining [21]. The CH_4 EF covers emissions from oil production, transport and refining [21,47].

[c] Natural gas: The CO_2 EF is based on the conventional and unconventional CO_2 EFs [22], calculated based on the year 2012 ratio of conventional to unconventional natural gas production [2]. The CH_4 EF covers upstream (conventional and unconventional) and downstream emissions from the EPA 1996, Howarth 2011 and Hultman 2011 publications, and is calculated based on the year 2012 ratio of conventional to unconventional natural gas production [2].

Upper limit of CH_4 leakage in natural gas production

As discussed in Section Introduction, there is a high level of uncertainty surrounding CH_4 leakage rates in natural gas production. Therefore, it was determined what the upper limit of CH_4 leakage in natural gas production is that would lead to the same CO_2-eq emissions in *H_2Econ* as in the baseline. The CH_4 leakage limit was determined by performing an optimization, in which the same natural gas production CH_4 leakage rate was applied to the baseline and to *H_2Econ* and adjusted until the CO_2-eq emissions were the same in both scenarios.

Methane cracking efficiency

Throughout the previous scenarios, an energy conversion efficiency of 55% was assumed for the methane cracking process based on estimations from the literature [14]. The energy conversion efficiency for the methane cracking process is defined here as the ratio between the energy output in terms of H_2 and the energy input in terms of CH_4, where CH_4 also supplies energy to overcome the reaction barrier ($\Delta H^0 = 74.85$ kJ/mol). However, methane cracking has not yet been implemented on a commercial scale and so the efficiency that will be realized in practice is not yet known. In order to further explore the MC-H_2 economy, the minimum required methane cracking efficiency was determined. This was done by performing an optimization, in which the same efficiency was applied to the baseline and *H_2Econ* and adjusted until the CO_2-eq emissions were the same in both scenarios.

Model

The methane cracking – hydrogen economy (MC-H_2) model was developed in order to implement the scenarios described in Section Scenarios, quantifying the effect of changes in H_2 production and road transportation on CO_2 and CH_4 emissions. The model quantifies anthropogenic emissions on the global scale from the sectors of relevance to the industrial use of hydrogen and the road transportation sector. Namely, global CO_2 emissions include emissions from production of coal, oil, and natural gas, as well as their use in industry, transport, buildings (residential, services and non-specified other) and other (agriculture and non-energy use), but exclude electricity and heat generation emissions. CO_2 emissions from electricity generation are only considered for electricity requirements for electrolysis in H_2 production. Global CH_4 emissions include stationary and combustion, oil and natural gas, coal mining, and biomass.

The MC-H_2 model is based on a series of input parameters and equations. The structure of the model is based on various aspects of the energy sector that are required to quantify changes in CO_2 and CH_4 emissions resulting from implementation of a H_2 economy. These aspects are referred to here as domains; in total, the model is made up of 17 domains. The model domains and the information flow in the model are shown in Fig. 1. A full description of the model is given in Weger 2015 [16].

Model evaluation

The MC-H_2 model was evaluated by a sensitivity analysis and subsequently calibrated. This evaluation is described in detail in Weger 2015 [16]. The parameters shown to have the greatest sensitivity are production of both oil and natural gas. The upper-end CH_4 EF value for oil production led to a 200% increase in CO_2-eq emissions, whereas the upper-end CH_4 EF value for upstream unconventional natural gas production led to a 35% increase in emissions. The considerable sensitivity observed here is due to wide uncertainty ranges in the EFs for production of both oil and natural gas. Calibration of the model is described in detail in Weger 2015 [16].

Data

Activity data

Activity data represent the amount of fuel consumption associated with a specific activity. The activity data used in this model were retrieved from the IEA. The data represent activity from the year 2012. The IEA activity data used in MC-H_2 represent total final consumption (TFC) energy, excluding electricity and heat. TFC includes industry, transport, buildings (residential, services and non-specified other) and other (agriculture and non-energy use) [2]. The demand for saleable fuel for combustion is treated as equivalent to the fuel pre-production to simplify calculations.

Emission factors

EF's represent the average emissions released per unit of given activity, and are typically provided as a range. The EFs used in the model were primarily retrieved from the 2006 IPCC Guidelines [21]. When data could not be retrieved from the IPCC, the data were obtained from alternative sources, as listed in Table 6.

Emissions and CH_4 global warming potential

CO_2 and CH_4 emissions are presented in units of CO_2 equivalent (CO_2-eq). CO_2-eq emissions are calculated by multiplying CH_4 emissions by the GWP of CH_4, and adding this value to the CO_2 emissions. The GWP measures the relative heat-trapping ability of CH_4 compared to CO_2, and is a function of the time frame considered after a pulse emission of CH_4. The high warming potential of CH_4 is primarily due to its strong absorption of infrared radiation emitted from the Earth's surface. Common time intervals to discuss the GWP of CH_4 are 20 and 100 years; CH_4 has a much larger 20-year GWP, because its atmospheric lifetime is about 12 years, while CO_2 has an effective influence on the atmosphere for about a century [4,20]. The 20-year GWP of CH_4 is 86, while the GWP drops to 34 over 100 years. The shorter, 20-year time scale for the GWP is more relevant and appropriate because of the urgent need to reduce CH_4 emissions in the next decades, so as to prevent climate tipping points such as the melting of permafrost, and to slow the rate of global warming. Therefore it is the 20-year GWP that was used here to convert CH_4 to CO_2-eq emissions.

Methodological approach

The Tier 1 approach from the *2006 IPCC Guidelines* was employed to calculate emissions [21]. In this approach, emissions are estimated based on the quantities of fuel combusted (activity data, AD) and globally-averaged EFs for a particular energy

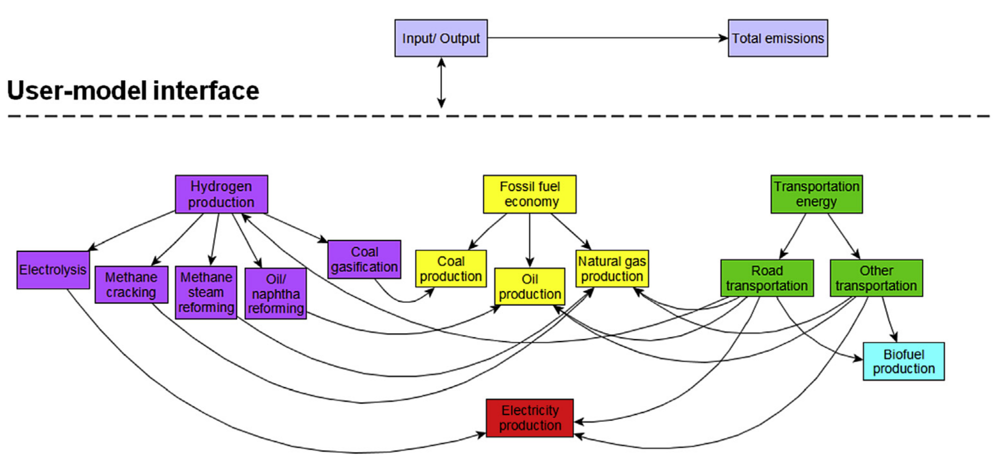

Fig. 1 – Schematic of the MC-H_2 model domains. The arrows follow the flow of energy demand from end-use applications to the point of energy production. The main component groups in MC-H_2 are H_2 (purple), fossil fuels (yellow), and transportation (green)

Table 6 – Emission factor data sources used in MC-H_2.

Domain	Parameter	Source
Fossil fuel economy	Coal	IPCC [21]
	Oil	IPCC [21]
	Natural gas	IPCC [21]
Road transportation	Oil	IPCC [21]
	Natural gas	IPCC [21]
	Electricity	–
	Biofuels	IPCC [21]
	Hydrogen	Wokaun and Wilhelm [42]
Coal production	Underground mining	IPCC [21]
	Underground post-mining	IPCC [21]
	Surface mining	IPCC [21]
	Surface post-mining	IPCC [21]
Coal gasification	Process	IPCC [21]
Oil production	Oil well	IPCC [21]
	Oil production	IPCC [21]; Cai [47]
	Oil transport	IPCC [21]
	Oil refining	IPCC [21]
Oil/naphtha reforming	Process	IPCC [21]
Natural gas production	Upstream conventional	EPA [23]; Hultman [38]; Howarth [22]
	Upstream unconventional	EPA [23]; Hultman [38]; Howarth [22]
	Downstream	EPA [23]; Hultman [38]; Howarth [22]
Methane cracking	Process	IPCC [21]
Methane steam reforming	Process	IPCC [21]
Biofuel production	Process	Mortimer [48]; Cai [47]
Electricity production	Process	IEA [49]; Ecometrica [50]
Electrolysis	Process	–

form/application, where emissions = $AD_{fuel} \times EF_{GHG,\,fuel}$. CO_2 EF's are primarily dependent on the carbon content of the fuel because the majority of the carbon will be oxidized to CO_2, meaning that globally-averaged CO_2 EFs do not introduce considerable uncertainty. On the other hand, CH_4 EF's are dependent on factors subject to variability, i.e., combustion technology and operating conditions, meaning that globally-averaged CH_4 EFs lead to relatively high uncertainty (for more information, refer to the *2006 IPCC Guidelines*).

Results and discussion

Industrial H_2

In this scenario set, *Industrial H_2*, conventional fossil fuel-based technologies are replaced with methane cracking for industrial H_2 production as explained in Section Scenarios. This generally leads to a decrease in CO_2-eq emissions; however, the achieved emissions decrease is low, within the range of 0–3.8%. The results are displayed in Table 7 and Fig. 2.

The main reason for the low emissions decrease is that the combined CO_2 and CH_4 EFs from natural gas production are higher than from coal and oil production (see Table 5), which curtails the emissions reductions achieved through methane cracking (see Table 2) from its zero-CO_2 emissions. The emissions decrease is greatest when the EPA 1996 EFs are applied and lowest when the Howarth 2011 EFs are applied. This is due to the combined CO_2 and CH_4 EFs being lowest with EPA 1996 and the highest with Howarth 2011. Furthermore, the decrease in emissions is greater when the natural gas supply used in the methane cracking process is 100% conventional, and lower when the natural gas supply is 100% unconventional. This is because the EFs for CO_2 and CH_4 combined are greater during unconventional natural gas production than conventional natural gas production. Furthermore, in the Howarth 2011 *Industrial H_2* scenario supplied with 100% unconventional gas, no change in CO_2-eq emissions is observed. In this scenario, the Howarth CH_4 leakage rate from unconventional natural gas production is high enough that it completely offsets the decrease in CO_2 emissions achieved through methane cracking. On the other hand, the EPA 1996 and Hultman 2011 EFs for CH_4 leakage from unconventional natural gas production are low enough so that they still lead to emissions reductions in their corresponding *Ind H_2 Full Pen* scenarios. This underlines that the effectiveness of methane cracking in reducing emissions from industrial H_2 production is dependent on the leakage rate of CH_4 in natural gas production.

RoadTrans H_2

In the next scenario set, *RoadTrans H_2*, oil and natural gas are fully replaced with H_2 produced by methane cracking to cover the energy needs in road transportation as explained in

Table 7 – Total global emissions of carbon dioxide and methane (Mton CO_2-eq) from the baseline and from the Industrial H_2 scenario. Emissions are calculated for supply with 100% conventional and for 100% unconventional natural gas.

Data source for natural gas production EFs	Scenario	Total emissions [Mton CO_2-eq][a]	
		Conventional natural gas	Unconventional natural gas
EPA 1996	Baseline	26 000	26 000
	Industrial H_2	25 000	25 000
	Change %	*−3.8%*	*−3.8%*
Hultman 2011	Baseline	27 000	29 000
	Industrial H_2	26 000	28 000
	Change %	*−3.7%*	*−3.4%*
Howarth 2011	Baseline	29 000	31 000
	Industrial H_2	28 000	31 000
	Change %	*−3.4%*	*0%*

The italics represent the % change in emissions from the baseline to the Industrial H_2 scenario.
[a] CO_2-eq for CH_4 over 20 years, with a GWP value of 86 [4].

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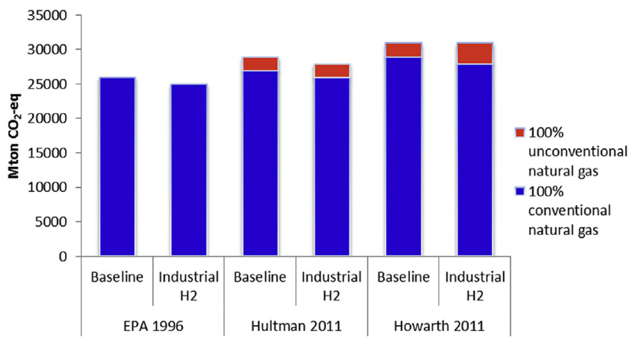

Fig. 2 – Total global emissions of carbon dioxide and methane (Mton CO_2-eq). 100% conventional natural gas (in blue), represents the total emissions incurred from 100% conventional natural gas supply. 100% unconventional natural gas (in red), represents the additional emissions incurred from 100% unconventional natural gas supply.

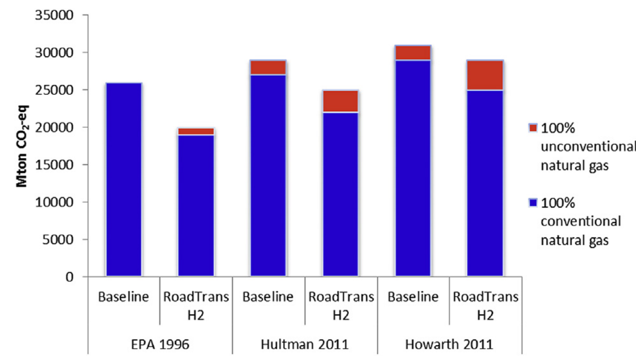

Fig. 3 – Total global emissions of carbon dioxide and methane (Mton CO_2-eq). 100% conventional natural gas (in blue), represents the total emissions incurred from 100% conventional natural gas supply. 100% unconventional natural gas (in red), represents the additional emissions incurred from 100% unconventional natural gas supply.

Section Scenarios. This consistently leads to a decrease in CO_2-eq emissions, and in some scenarios substantially so, within the range of 6.5–27%. This wide range results from the different CH_4 leakage rates applied in the scenarios, and will be explained in greater detail below. The results are displayed below in Table 8 and Fig. 3.

The trends observed in the *Industrial H_2* scenarios were generally observed in the *RoadTrans H_2* scenarios as well. Namely, the emissions decrease is greatest when applying the EPA 1996 EFs and least when applying the Howarth 2011 EFs, and the emissions decrease is greater when natural gas supply is 100% conventional, and less when it is 100% unconventional. The explanations for these observations are discussed in the previous section. However, differences are also observed between the scenario sets. First, the magnitude of the emissions decrease is substantially greater among the *RoadTrans H_2* scenarios compared to the *Industrial H_2* scenarios (6.5–27% CO_2-eq emissions reductions in the *RoadTrans H_2* scenarios compared with 0–3.8% *Industrial H_2* scenarios). The main reason for the is that the *RoadTrans H_2* scenarios require substantially less fuel in road transportation compared to the baseline and *Industrial H_2* scenarios. This is because the efficiency of the H_2 fuel cell is more than twice as high as that of the petrol/diesel ICE, which essentially reduces the road transportation fuel demand by half. Second, the range of emissions decrease is greater in the *RoadTrans H_2* scenarios compared to the *Industrial H_2* scenarios. The wide range of emissions decrease is due to the varying CH_4 leakage rates used, which have a more pronounced impact on total emissions in the *RoadTrans H_2* scenarios than in the *Industrial H_2* scenarios. This is because more natural gas is needed in total in the *RoadTrans H_2* scenarios to provide H_2 fuel by methane cracking for road transportation. Third, the Howarth *Industrial H_2* scenario utilizing 100% unconventional natural gas leads to no change in emissions, while the Howarth *RoadTrans H_2* scenario utilizing 100% unconventional natural gas leads to a net decrease in emissions. One of the main reasons an emissions decrease was calculated in the latter scenario is due to the significant decrease in road transportation fuel demand. Nevertheless, the emissions decrease in this scenario is low, at 6.5%, which indicates that the very high CH_4 leakage rate from unconventional natural gas production provided by Howarth 2011 is close to the limit at which the increase in CH_4 emissions due to increased gas production cannot be compensated by the decrease in CO_2 emissions achieved through methane cracking. This emphasizes the importance of CH_4 emissions in natural gas production on climate benefits through emissions reductions achieved in the *RoadTrans H_2* scenarios.

Table 8 – Total global emissions of carbon dioxide and methane (Mton CO_2-eq) from the baseline and from the RoadTrans H_2 scenario. Emissions are calculated for supply with 100% conventional and for 100% unconventional natural gas.

Data source	Scenario	Total emissions [Mton CO_2-eq][a]	
		Conventional natural gas	Unconventional natural gas
EPA 1996	Baseline	26 000	26 000
	RoadTrans H_2	19 000	20 000
	Change %	*−27%*	*−23%*
Hultman 2011	Baseline	27 000	29 000
	RoadTrans H_2	22 000	25 000
	Change %	*−18%*	*−14%*
Howarth 2011	Baseline	29 000	31 000
	RoadTrans H_2	25 000	29 000
	Change %	*−14%*	*−6.5%*

The italics represent the % change in emissions from the baseline to the RoadTrans H_2 scenario.
[a] CO_2-eq for CH_4 over 20 years, with a GWP value of 86 [4].

Pessimistic RoadTrans H_2

In the next scenario, *Pessimistic RoadTrans H_2*, H_2 fuel replaces oil and natural gas in the road transportation sector, under pessimistic assumptions as explained in Section Scenarios. With 100% conventional natural gas supply, CO_2-eq emissions increase by 19% from the baseline to the *Pessimistic RoadTrans* H_2 (from 31,000 to 37,000 Mton CO_2-eq), and with 100% unconventional natural gas supply CO_2-eq emissions increase by as much as 27% (from 33,000 to 42,000 Mton CO_2-eq). The results are shown in Fig. 4.

The results underline the critical role of assumptions in whether the H_2 economy has a beneficial or detrimental impact on the climate through emissions. Namely, pessimistic assumptions as applied here, including the production of H_2 by high-emissions-generating methane steam reforming, relatively high CH_4 leakage rates from natural gas production, and a low tank-to-wheel efficiency of H_2 through use of a H_2 internal combustion engine, result in a significant and unfavorable impact on the climate through emissions increase. On the other hand, optimistic assumptions such as the production of H_2 by low-emissions-generating methane cracking, relatively low CH_4 leakage rates from natural gas production, and a high tank-to-wheel efficiency of H_2 by way of a H_2 fuel cell enable climate benefits through emissions reduction. Thus, the H_2 economy can lead to net reduction of GHG emissions, but only if a low-emissions-generating H_2 production technology like methane cracking is applied, if CH_4 emissions from natural gas production are low, and a high tank-to-wheel efficiency of H_2 (i.e., application of the H_2 fuel cell) is possible.

Elemental carbon production from methane cracking

In this section, the elemental carbon produced by methane cracking is quantified in the *Industrial* H_2 and *RoadTrans* H_2 scenarios as explained in Section Scenarios. In the *Industrial* H_2 scenario, 170 Mton carbon is produced by methane cracking. On the other hand, 790 Mton carbon is produced by methane cracking in the *RoadTrans* H_2 scenario, which amounts to 4.5 times more carbon production than in the *Industrial* H_2 scenario. This is due to the fact that much more H_2 is required to be produced by methane cracking in the road transportation sector than in the industrial H_2 sector. If the carbon produced from methane cracking can be later used as a commodity in commercial applications, this would reduce life cycle emissions incurred from carbon production [45].

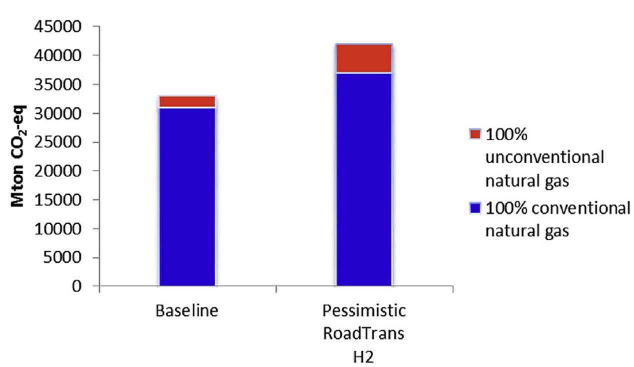

Fig. 4 – Total global emissions of carbon dioxide and methane (shown in Mton CO_2-eq). 100% conventional natural gas (in blue), represents the total emissions incurred from 100% conventional natural gas supply. 100% unconventional natural gas (in red), represents the additional emissions incurred from 100% unconventional natural gas supply.

Hydrogen emissions

In this section, H_2 emissions from H_2 fuel use in road transportation under the *RoadTrans* H_2 scenario are quantified and compared to estimates on current H_2 emissions from incomplete combustion of oil and natural gas in road transportation, as explained in Section H_2 emissions. The results are displayed in Fig. 5. In the *RoadTrans* H_2 scenario, a H_2 leakage rate of 1% results in 2.6 Mton H_2 emissions per year, while a H_2 leakage rate of 2% results in 5.4 Mton H_2 emissions per year (explained in Section H_2 emissions). These values are comparable to current emissions in the literature [2,42], from which extrapolated H_2 emissions based on the increase of oil and natural gas in road transportation for year 2012 are 4.75 Mton [2]. Therefore, with full penetration of H_2 fuel in road transportation, H_2 emissions stay roughly the same, changing by −2.15 to +0.65 Mton H_2 per year. Based on the modest change in H_2 emissions resulting from replacing oil and natural gas with H_2 fuel, it is unlikely that H_2 fuel use under the *RoadTrans* H_2 scenario would lead to a considerable direct effect on OH. Because OH controls the atmospheric lifetime of GHGs and pollutants through oxidation, it is therefore unlikely that the lifetimes of these species would change to an appreciable extent. However, global-scale replacement of the ICE with the H_2 fuel cell may significantly decrease NO_x emissions [41]. This is because NO_x is generated from the nitrogen and oxygen present in ambient air during fuel combustion due to the high temperatures reached. Decreased NO_x emissions would have an indirect effect of reducing OH, which in turn would reduce OH's global oxidizing capacity of trace gases. Nevertheless, a reduction in NO_x emissions would improve human and environmental health through reduction of tropospheric O_3 formation, since tropospheric O_3 is a powerful air pollutant.

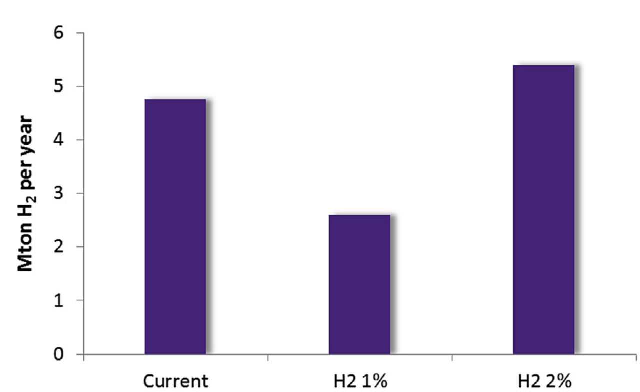

Fig. 5 – Hydrogen emissions (Mton H_2) from road transportation. "H_2%" refers to the specific hydrogen leakage rate applied from hydrogen fuel use in the RoadTrans H_2 scenarios.

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CH_4 leakage limit in natural gas production

In this section, the upper limit of CH_4 leakage in natural gas production is determined as explained in Section Scenarios. It was found that with 100% conventional natural gas supply, the upper limit of CH_4 leakage is 7.1% combined for upstream and downstream CH_4 emissions. With 100% unconventional natural gas supply, the CH_4 leakage limit is 7.0% combined for upstream and downstream CH_4 emissions. The limit is slightly higher for 100% conventional natural gas supply because CO_2 emissions from conventional natural gas production are less than from unconventional natural gas production. While the EPA 1996, Howarth 2011 and Hultman 2011 natural gas production leakage rates are well under the CH_4 leakage limits presented here, higher natural gas leakage rates have been reported in the literature [20,25,27–30,33]. In fact, the upper-end CH_4 leakage rate for unconventional natural gas production for upstream and downstream combined, from Howarth et al. 2011 [22], is as high as 7.9%. It is also noteworthy that these EFs were measured for natural gas production in the US, and EFs may be higher in countries with less stringent regulations, perhaps substantially so. Ensuring that the globally averaged CH_4 leakage rate from natural gas production is below the CH_4 leakage limits presented here is decisive in the MC-H_2 economy providing climate benefits.

Required methane cracking efficiency

In this section, the minimum required methane cracking efficiency above which the MC-H_2 economy provides net climate benefits is determined as explained in Section Scenarios. The results are displayed below in Table 9. The analysis reveals that the minimum required methane cracking efficiency strongly varies based on the CH_4 leakage rate from natural gas production. Most notably, the minimum required methane cracking efficiency for each CH_4 EF used here, and for both 100% conventional and 100% unconventional natural gas supply, are all well under the 55% energy efficiency mark postulated in the literature as an achievable value on the commercial scale. Of course, with higher CH_4 leakage rates from natural gas production, an even higher methane cracking efficiency would be required than the ones displayed in Table 9. Nevertheless, this result is promising for the MC-H_2 economy, provided that CH_4 leakage rates from natural gas production do not greatly exceed those of Howarth 2011.

Table 9 – Minimum required efficiency of methane cracking so that CO_2-eq emissions from the H_2Econ scenario are equal to those from the baseline scenario. Emissions are calculated for 100% conventional natural gas supply and for 100% unconventional natural supply.

Data source[a]	Required methane cracking efficiency[b]	
	Conventional natural gas	Unconventional natural gas
EPA 1996 [23]	11%	12%
Hultman 2011 [38]	20%	32%
Howarth 2011 [22]	33%	47%

[a] Source of EF data set for CH_4 leakage in natural gas production.
[b] Efficiency from providing energy for the reaction to proceed, and pressurizing the reaction vessel.

Conclusion and outlook

The results presented here support the proposition that a fossil-fuel-enabled bridge to a fully renewable-based H_2 economy can bring benefits to the climate through reduction of CO_2-eq emissions. However, the impact of the MC-H_2 economy on emissions is highly dependent on the factors facilitating it. Optimistic assumptions, including the production of H_2 by methane cracking, relatively low CH_4 leakage rates from natural gas production, and a high tank-to-wheel efficiency of H_2 by way of a H_2 fuel cell enable climate benefits through emissions reduction. On the other hand, pessimistic assumptions such as the production of H_2 by conventional, fossil-based, high-emission technologies like methane steam reforming, relatively high CH_4 leakage rates from natural gas production, and a high tank-to-wheel efficiency of H_2 through use of a H_2 internal combustion engine, result in an unfavorable climate impact through considerable emissions increase.

In order to achieve net CO_2-eq emissions decrease with the MC-H_2 economy, it is important that the globally-averaged CH_4 leakage rates from natural gas production are below 7%, and even lower for more substantial emissions reductions to be realized (see Section CH_4 leakage limit in natural gas production, Industrial H_2 and RoadTrans H_2). However, higher CH_4 leakage rates have been reported in the literature [20,25,27–30,33]. Nevertheless, some of these very high CH_4 leakage rates were observed in areas where high CH_4 fluxes were expected, and are not necessarily representative of typical CH_4 leakage rates on a large scale [20]. In any case, due to the high degree of uncertainty surrounding the CH_4 leakage rates, further research is required in order to form more robust and consistent CH_4 EF estimates for natural gas production.

Methane cracking and the H_2 fuel cell are likewise needed to achieve net CO_2-eq emissions decrease with the MC-H_2 economy. Both of these technologies require further research and development in order to become realized on the global scale. Additionally, it is important to determine the energy conversion efficiency of methane cracking as well as the tank-to-wheel efficiency of a commercialized hydrogen fuel cell that could be realistically achieved, so as to determine the impact of the MC-H_2 economy on emissions. It would also be interesting to explore the effect of centralized H_2 production on the MC-H_2 economy because this would avoid downstream CH_4 emissions, which in turn may lead to lower CH_4 emissions.

Based on the sensitivity results, more study is needed to better understand CH_4 leakage from oil production (see Section Model evaluation). Due to the high uncertainty in CH_4 emissions from oil production, the potential impact of this sector on global CO_2-eq emissions is considerable. It is important that the uncertainty in CH_4 leakage from natural gas production does not overshadow the considerable uncertainty of the CH_4 leakage rate from oil production. More research is required to understand oil's true impact on the climate, which may be far worse than what is currently perceived.

If the MC-H_2 economy is implemented, caution is advised to prevent technological lock-in into a natural gas fossil fuel economy, and to prevent a delay in the shift of the energy system to renewables. Instead, the MC-H_2 economy can potentially serve as a bridge to a renewable H_2 economy, in which it facilitates development of the H_2 economy infrastructure, if in the process it can provide climate benefits through reduced CO_2-eq emissions.

An important aspect missing from this work is the cost competitiveness of the MC-H_2 economy. While the MC-H_2 economy may have the ability to significantly mitigate emissions, it would never be realized if it is not economically feasible. In this context it would be interesting to consider the economic potential of the elemental carbon produced by the methane cracking process. Therefore, more research is needed to explore the financial considerations of MC-H_2.

Finally, while the results presented here support the MC-H_2 economy's potential in benefitting the climate through reduction of CO_2-eq emissions, there are other aspects not considered in this work that may have important environmental consequences. For instance, increased shale gas production without effective environmental regulations on a global scale may negatively impact human and environmental health by degrading air quality and contaminating drinking water. It is important that future research into the MC-H_2 economy consider comprehensive potential environmental consequences of increased shale gas production, lest certain environmental goals be achieved while others are sacrificed.

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