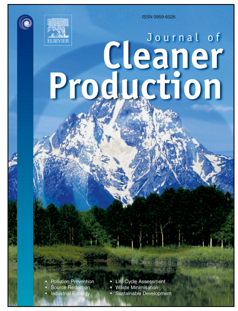
Accepted Manuscript



Life cycle greenhouse gas emissions and freshwater consumption of liquefied Marcellus shale gas used for international power generation

Dharik S. Mallapragada, Eric Reyes-Bastida, Frank Roberto, Erin M. McElroy, Dejan Veskovic, Ian J. Laurenzi

PII: S0959-6526(18)32831-2

DOI: 10.1016/j.jclepro.2018.09.111

Reference: JCLP 14246

To appear in: *Journal of Cleaner Production*

Received Date: 29 June 2018

Revised Date: 13 August 2018

Accepted Date: 13 September 2018

Please cite this article as: Mallapragada DS, Reyes-Bastida E, Roberto F, McElroy EM, Veskovic D, Laurenzi IJ, Life cycle greenhouse gas emissions and freshwater consumption of liquefied Marcellus shale gas used for international power generation, *Journal of Cleaner Production* (2018), doi: https://doi.org/10.1016/j.jclepro.2018.09.111.

Word count: 8025

Life cycle greenhouse gas emissions and freshwater consumption of liquefied Marcellus shale gas used for international power generation

Dharik S. Mallapragada[1], Eric Reyes-Bastida[1], Frank Roberto[1], Erin M. McElroy[2], Dejan Veskovic[3], and Ian J. Laurenzi[1]

1. ExxonMobil Research and Engineering Company

2. SeaRiver Maritime

3. Air Products and Chemicals, Inc.

Abstract

The recent growth in U.S. natural gas reserves has led to interest in exporting liquefied natural gas (LNG) to countries in Asia, Europe and Latin America. Here, we estimate the life cycle greenhouse gas (GHG) emissions and life cycle freshwater consumption associated with exporting Marcellus shale gas as LNG for power generation in different import markets. The well-to-wire analysis relies on operations data for gas production, processing, transmission, and regasification, while also accounting for the latest measurements of fugitive CH_4 emissions from U.S. natural gas activities. To estimate GHG emissions from a typical U.S. liquefaction facility, we use a bottom-up process model that can evaluate the impact of gas composition, technology choices for gas treatment and on-site power generation on overall facility GHG emissions. For LNG exports to Mumbai, India for power generation in a combined cycle power plant with 50% efficiency, the base case life cycle GHG emissions, freshwater consumption, and CH_4 emissions as fraction of gross gas production are estimated to be 473 kg CO_2eq/MWh (80% confidence interval: 452 - 503 kg CO_2eq/MWh), 243 gal/MWh (80% CI: 200 - 300 gal/MWh) and 1.2% (80% CI: 0.81 - 1.79%), respectively. Among all destinations considered, typical life cycle GHG emissions range from 459 kg CO_2eq/MWh to 473 kg CO_2eq/MWh, with GHG emissions from liquefaction, shipping and regasification contributing 7 - 10% of life cycle GHG emissions.

Significance Statement

In late 2017, the United States became a net exporter of natural gas due to the growth of liquefied natural gas (LNG) export facilities. With multiple LNG plants scheduled to begin operating in 2018, assessment of the environmental impacts of U.S. LNG is timely. Unlike LNG plants in most other countries, where liquefaction is integrated with the treatment and processing of "raw" natural gas from the subsurface, U.S. facilities liquefy pipeline-quality gas. To understand the greenhouse gas (GHG) emissions and freshwater consumption associated with this unique supply chain, we have conducted the first comprehensive life cycle assessment (LCA) of LNG sourced from Marcellus gas, utilizing production data from XTO Energy, recently published data on midstream methane emissions by the Environmental Defense Fund, and engineering data specific to U.S. LNG facilities from Air Products and UOP, establishing robust estimates of the footprint of current production and liquefaction practices..

1. Introduction

In less than a decade, shale gas production in the United States has grown rapidly, going from 5% to over 50% of annual natural gas (NG) production from 2005 to 2015 [1]. The increased gas supply available from shale gas, made possible through advances in horizontal drilling and hydraulic fracturing technologies, has contributed to increased domestic NG consumption, going from 22 trillion cubic feet (tcf) in 2005 to 27 tcf in 2015. Yet, with the likely continued growth in shale gas production, it is projected that U.S. will become a net exporter of gas by around 2018, with liquefied natural gas (LNG) expected to be the dominant mode of export [1]. LNG enables the long-distance transport of NG to distant markets in Europe, Latin America and Asia, where it is expected to be used for power generation, heating and transportation, among other purposes.

In recent years, a number of life cycle assessments (LCAs) have investigated the greenhouse gas (GHG) emissions and freshwater consumption associated with the shale gas life cycle, from drilling and completion to use as a fuel at a U.S.-based power plant [2, 3, 4, 5, 6, 7]. Moreover, several investigations organized by the Environmental Defense Fund have attempted to quantify CH_4 emissions from various stages of the gas life cycle [8, 9, 10], developing sectorial emission inventories [8, 10] and analyzing the life cycle GHG impact of using shale gas for various end uses, again, in the U.S. context [11, 12, 13].

By contrast, investigations of the life cycle impacts of shale gas exported as LNG from the U.S. to other countries are relatively sparse. In 2014, the National Energy Technology Laboratory (NETL) [14], estimated the life cycle GHG emissions of LNG exports to Europe (Rotterdam) and Asia (Shanghai) for electricity production to be 629 kg CO_2eq/MWh and 660 kg CO_2eq/MWh, respectively. The following year, Abrahams and coworkers [15] estimated mean life cycle GHG emissions of exporting U.S. LNG to Europe and Asia to be 655 kg CO_2eq per MWh electricity, with ~11% of the life cycle GHG emissions coming from with the LNG supply chain . More recently, Raj and coworkers estimated the life cycle GHG emissions for exporting Canadian shale gas to China for power generation, with a particular focus on the sensitivity of the life cycle GHG emissions to the choice of shale play from where the gas is sourced [16].

In this work, we have quantified the life cycle GHG emissions and freshwater consumption associated with the shale gas life cycle whereby gas is exported as LNG to locations around the world for use in power generation. The destinations of exported LNG considered in this study are among the top LNG importing countries as of 2015 – Japan (1^{st}), India (4^{th}), the UK (6^{th}) and Spain (7^{th}) and Chile (15^{th}) [17]. The LCA is based on gas produced from the Marcellus shale and relies on new field data gathered from ExxonMobil operations to quantify the GHG emissions associated with natural gas drilling, hydraulic fracturing, gas gathering systems and processing. Furthermore, we employ the latest estimates of CH_4 emissions associated with gas production, processing, and transmission, as measured and quantified by the aforementioned studies coordinated by the Environmental Defense Fund [8, 9, 10]. We also report the first bottom-up process modeling approach to estimate GHG emissions associated with U.S.-based LNG plants, including gas treatment, liquefaction, and LNG storage. This approach enabled evaluation of the impacts of gas composition and technology choices for gas processing, liquefaction and on-site power generation on both LNG-facility GHG emissions as well as the life cycle GHG emissions of U.S. LNG, which have not been considered by previous peer-reviewed LCAs of U.S. LNG. We also explicitly evaluated the sensitivities of the life cycle impacts of LNG to various modes of LNG marine transportation, including impacts of alternative tanker capacities and on-board reliquefaction. We conclude by qualitatively comparing the findings of this study and those of prior LCA studies on U.S. LNG exports.

2. Methods

As the purpose of this study is to assess all GHG emissions and freshwater consumption from “cradle to grave”, we adopted the “system boundary” of Laurenzi and Jersey (2013) for this LCA and added operations associated with natural gas liquefaction, shipping, regasification, and gas pipeline transportation downstream of regasification. A succinct depiction is provided in Figure 1. The system boundary includes the life cycle impacts of purchased power, steel and cement employed for Marcellus wells, proppant, additives and fuel employed for hydraulic fracturing, and fuel employed for drilling, and marine transportation. The end of the gas life cycle is a combined cycle gas turbine (CCGT) consisting of two F-class turbines and two HRSGs with a total plant efficiency of 50.2% (HHV basis) [21]. We employ a “functional unit” of 1 MWh of power generated at the power plant to facilitate comparisons with other forms of power generation technology. Following the recommendations of the Kyoto protocol [35], we quantify emissions of CO_2, CH_4 and N_2O in terms of CO_2-equivalents using a 100-year global warming potential (GWP). For this study, we employed GWPs reported in the fifth IPPC assessment report (AR5) [18], i.e. 30 kg CO_2eq/kg CH_4 and 265 kg CO_2eq/kg N_2O. In the supplemental information (SI), we also report our findings in terms of 20-year GWPs from the IPCC AR5.

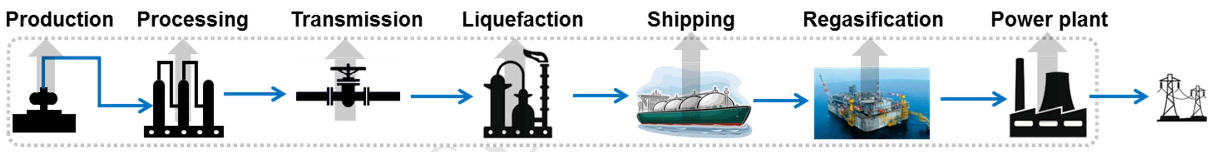


Figure 1. System boundary defined for LCA of shale gas exported as LNG for power generation. The stages of production, processing and transmission are referred as the domestic gas supply chain. The stages of liquefaction, shipping and regasification are referred as the LNG supply chain.

The production stage of the life cycle includes impacts associated with drilling, hydraulic fracturing and flowback, and gas production as well as the collection, transport and Class II disposal of produced water. We employed an approach similar to Laurenzi and Jersey (2013), with a few key distinctions:

1. We employed the CH_4 emission factors for chemical injection pumps, pneumatic (level) controllers, and “Upstream Equipment Leaks” reported by the UT/EDF study [8].
2. We employed the CH_4 emission factor for compressors and dehydration units that are part of the gathering system reported by Mitchell and coworkers [9] (Figure S2)
3. We employed updated data sets for Estimated Ultimate Recoveries (EURs), volumes of gas flared during flowback, water injected into the subsurface for hydraulic fracturing per well diesel fuel consumption for drilling and hydraulic fracturing operations, various purposes such as fracturing, drilling, transport of wastewater to disposal wells (Figure S1, Table S1). We also employed fuel consumption data specific to Marcellus shale gas compressor stations.

GHG emissions and freshwater consumption associated with the processing stage were modeled using natural gas and electricity consumption as well as NGL recovery data from XTO-operated facilities in the Marcellus region (Table S3 and Table S4). Fugitive emissions associated with gas processing were adopted from the measurements of Mitchell and coworkers, who reported data for16 processing plants in the U.S. [9].

Impacts associated with the gas transmission stage were assessed using an approach similar to Laurenzi and Jersey (2013). In this work, we employed the prevailing mix of prime movers (e.g. gas engine, gas turbine or electric motor, Table S5) at U.S. compressor stations in 2012, and employed their average utilization over the entire year as reported in compiled FERC form 2 data reported by Zimmerle and coworkers [10]. Fugitive CH_4 emissions for the transmission and storage sector in 2012 were also adopted from Zimmerle and coworkers [10]

Liquefaction, shipping and regasification collectively represent the LNG supply chain. In the U.S., liquefaction facilities process pipeline quality gas, which is largely free of higher value hydrocarbons (propane and larger) and impurities such as nitrogen, water, H_2S and CO_2. Nevertheless, pipeline quality gas requires additional treatment to remove trace quantities of H_2S and CO_2, water, and hydrocarbons larger than pentane (C_5+) that may freeze during liquefaction. For instance, the water and CO_2 concentrations must be reduced to 0.5 ppm and 50 ppm, respectively [36].

Impacts associated with the liquefaction facility were estimated via bottom-up process models of the liquefaction plant (Figure 2), including all gas treatment, liquefaction, power generation and storage operations. The models – based on GTPro data for gas turbine operations and ProSteam [37] modeling, explicitly accounted for mass and energy flows associated with each unit the entire facility. The process model takes as input: 1) data provided by equipment vendors on utility requirements (steam, electricity, heating or cooling needs) and extent of separation achieved in gas treatment units configured for North American liquefaction facilities and 2) choice of prime mover (e.g. gas turbine type or electric motor) and mechanical power requirements to operate refrigeration cycle for gas liquefaction, as per vendor provided information. This information is then used to estimate the mass flows across the various units, the LNG composition and total utility requirements needed by a facility producing 5 million metric tonnes per annum (MMtpa) LNG. The utility requirements were modeled to be provided by the balance of plant system, whose design includes gas turbines providing mechanical power for the refrigeration cycle, steam production from boilers and heat recovery from the gas turbine exhaust to provide the process heating and electricity needs (Figure S6). Systems to recover waste heat from gas turbine exhaust are commonly found in the design of liquefaction facilities being constructed in the U.S., either for generating steam and then electricity [26, 27, 30] or for providing heating to other process units [29, 28]. The boil-off gas generated from LNG storage tanks located onsite is used as fuel in the balance of plant system. The boil-off rates were estimated based on maximum capacity of tank volumes for a typical 5 MMtpa facility size (see section S4). Finally, any electricity generated in excess of the facility electric power needs is assumed to be exported to the local power grid. Additionally, we also included estimates of fugitive CH_4 emissions associated with liquefaction plants by using as proxy, data available for U.S. gas processing plants [9]. In the absence of CH_4 emissions data at liquefaction facilities, this approach is reasonable because many of the potential sources of CH_4 emissions at gas processing plants are also present at liquefaction facilities (e.g. gas treatment, compressors, dehydration etc.). Our analysis also includes an estimate of the potential GHG emissions from gas flaring during periods of operational upsets and maintenance at the liquefaction facility. We use the maximum flaring GHG emissions reported in the environmental assessment reports for four proposed U.S. liquefaction [30, 28, 29, 26] facilities to estimate the flaring emissions from a typical liquefaction facility (Table S8).

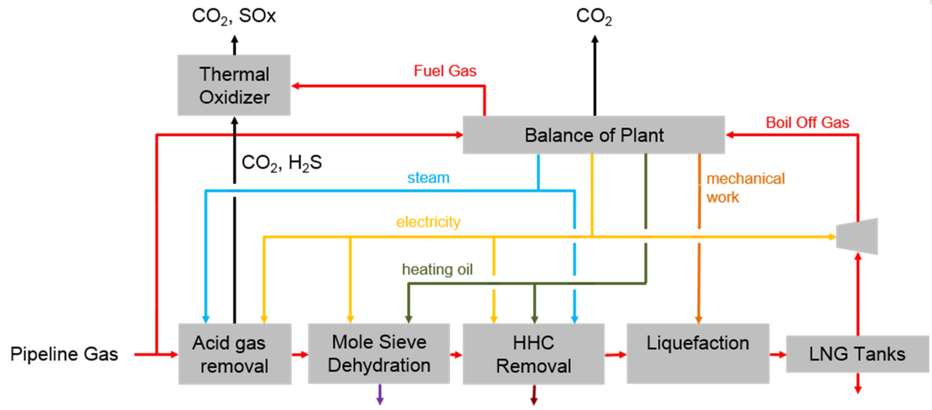


Figure 2. Process flow diagram of a typical liquefaction facility that is used to estimate the facility GHG emissions. The main electricity, steam and mass flows are indicated. C3 refrigeration is not shown (can be independent or siphoned from C3 part of the refrigeration cycle for the liquefaction unit), but applied to dehydration and HHC removal units. The cooled heating oil is returned to the utilities to be re-heated. Steam delivered to the HHC removal, and acid gas removal units is returned to utilities as condensed water. Even though there is infinitesimal amounts of H_2S in the Marcellus gas, it is included here for completeness. The thermal oxidizer operates irrespective of which gas goes through the plant. HHC = Heavy Hydrocarbons.

Using this model, we evaluated the effects of gas composition, waste heat recovery from the gas turbine exhaust, and alternative technologies for heavy hydrocarbon (HHC) removal (either cryogenic or adsorption based separation [38]) on facility GHG emissions and freshwater consumption.

Impacts associated with the shipping of LNG were estimated from the fuel consumption for LNG transport for different tanker configurations. We considered ships with and without the capability to re-liquefy boil-off gas, as well as alternative ship capacities (175,000 or 215,000 m^3). For each tanker configuration, the fuel consumption estimates associated with the modeled shipping routes account for different types and amounts of fuel used during each stage of the voyage, such as loading at port, laden at sea in an emission control area (ECA), canal passage (Suez or Panama), and return voyage. When passing through ECAs, the restrictions on fuel sulfur content require predominant use of fuels other than Heavy Fuel Oil (HFO) and this operational consideration is reflected in the GHG emissions and freshwater consumption estimated for the shipping stage (see S5). We also include estimates of methane slip associated with natural-gas marine engines used for LNG carriers [39].

Impacts associated with regasification were modeled based on the design of the Adriatic regasification terminal (Italy), which is operated by ExxonMobil [40]. LNG is vaporized by heat exchange with sea water as well as the exhaust gas from two on-site gas turbines, which supply the electric power needs of the facility. We estimated the fugitive CH_4 emissions associated with regasification by using as a proxy the values reported for gas processing plants, based on a similar rationale discussed above in the context of estimating fugitive CH_4 emissions from liquefaction plants.

The vaporized gas leaving the regasification terminal is sent to a pipeline network for all destinations except Japan (where we model the power plant as adjacent to the terminal). To assess the GHG emissions associated with non-U.S. pipeline operation downstream of the regasification terminal, we adopted the life cycle inventories recently reported by thinkstep [41]. These included electricity consumption, diesel consumption, and combustive and fugitive emissions for five (European) regions, based on data collected by (European) pipeline operators. In MC simulations, we uniformly randomly selected among these inventories.

The final stage of the gas life cycle is a combined cycle gas turbine featuring two F-class turbines, two heat recovery steam generators, and closed-loop cooling, yielding a typical efficiency 50% on a higher heating value (HHV) basis [42]. Although older CCGT machines may have lower efficiencies, and newer plants featuring H-class turbines may have higher efficiencies, the power plant efficiency we have employed is commonly employed in LCAs of natural gas ([23, 43, 22, 24]. We adopt the freshwater consumption associated with the closed-loop cooling system reported by the National Renewable Energy Laboratory [44].

Our LCA boundary does not include operations associated with construction and decommissioning of facilities for processing, liquefaction, re-gasification or power generation. The impacts associated with construction and decommissioning have been reported to as small relative to the impacts associated with operations [7].

The calculations for the LCA were performed using Microsoft Excel 2013 with the Oracle Crystal Ball 11 “Add in”, which enables sensitivity analyses and Monte Carlo simulation.

3. Results

3.1. Base Cases

The “base case” life cycle GHG emissions associated with Marcellus shale gas used for power generation in a variety of countries are illustrated in Figure 3, where “base case” emissions are those calculated using average values of data sets (e.g. average EURs, see Methods and Supporting information (SI)). Noteworthy technology choices associated with these life cycles include 1) grid-electricity powered compression of pipeline-quality gas departing the gas processing plant, 2) the use of Frame 7EA gas turbines coupled with heat recovery steam generators (cogeneration) at the liquefaction plant, 3) adsorption-based removal of heavy hydrocarbons from pipeline gas at the liquefaction facility and 4) shipping of LNG via 215,000 m^3 tanker featuring on-board reliquefaction.

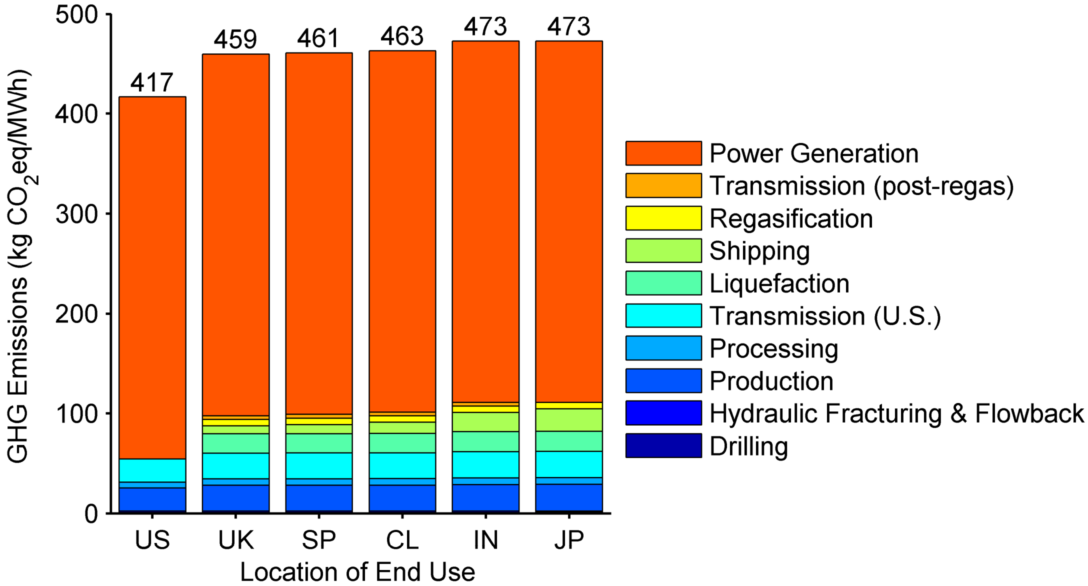


Figure 3 A breakdown of the life cycle GHG emissions associated with Marcellus shale gas used for power generations in various countries. US = United States, UK = United Kingdom, SP = Spain, CL = Chile, IN = India, JP = Japan. Marcellus shale gas is liquefied for transport to all non-U.S. locations. Results are reported using 100-year GWPs as reported by the 5th Assessment Report of the IPCC (GWP_{CH4} = 30, GWP_{N2O} = 265).

Our results show that LNG-specific operations (liquefaction, shipping and regasification) result in a 34 to 49 kg CO_2eq/MWh (10 to 13%) increase in the life cycle GHG emissions relative to a domestic-use scenario, depending upon the location at which the gas is used for power generation. GHG emissions arising from LNG-specific operations constitute 7 - 10% of the life cycle GHG emissions for all non-U.S. destinations. The predominant share of life cycle GHG emissions (77 - 79%) associated with using LNG for power generation occur at the power plant itself. Interestingly, the life cycle GHG emissions associated with U.S. LNG delivered to India and Japan are roughly equal, despite the difference in shipping distance. This is a consequence of the fact that Japanese natural gas CCGT plants are co-located with LNG terminals, i.e. the difference in GHG emissions associated with marine transport of LNG is offset by the absence of a large scale pipeline transport between the regasification and end use stages of the Japanese gas power life cycle.

In Figure 4 we provide a more detailed breakdown of the GHG emissions of LNG from the Marcellus shale play to Mumbai, excluding power generation ("Well to Plant"). The top five major sources of emissions, in descending order, are: 1) fuel consumption associated with shipping (18.8 kg CO_2eq/MWh), 2) fuel combustion at the liquefaction plant (16.3 kg CO_2eq/MWh), 3) fugitive CH_4 emissions associated with gas transmission (e.g. pipeline compressor stations, 13.3 kg CO_2eq/MWh), 4) fuel consumption for transmission compressor stations (12.5 kg CO_2eq/MWh) and 5) fuel consumption associated with gathering system compressor stations (10.2 kg CO_2eq/MWh). Overall, vented and fugitive CH_4 emissions is approximately 8% of the life cycle emissions on a CO_2-equivalent basis (100-year time horizon).

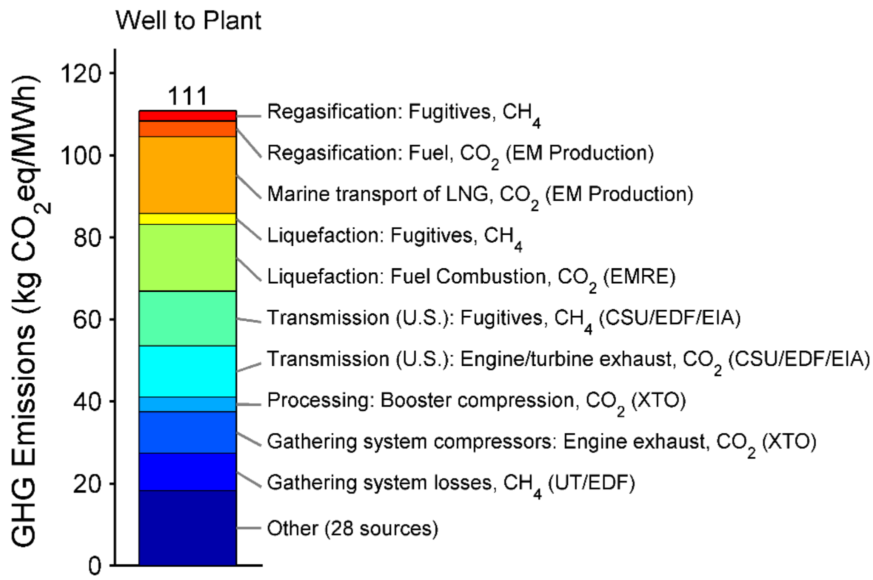


Figure 4. Breakdown of GHG emissions associated with Marcellus Shale gas exported as LNG to Mumbai (India) for power generation, excluding the power plant GHG emissions. A complete list of technology and parameter assumptions is available in supporting information (SI, Table S13). GHG reported using IPCC AR5 GWPs (100-year) [18]. The text parenthesis for each block in the well-to-plant GHG emissions plot refers to the source of data used. UT = University of Texas Austin, CSU/EDF = Environmental Defense Fund sponsored studies, EIA = U.S. Energy Information Administration, XTO = ExxonMobil subsidiary involved with production and processing of shale gas, EM = ExxonMobil, EMRE = ExxonMobil Research and Engineering.

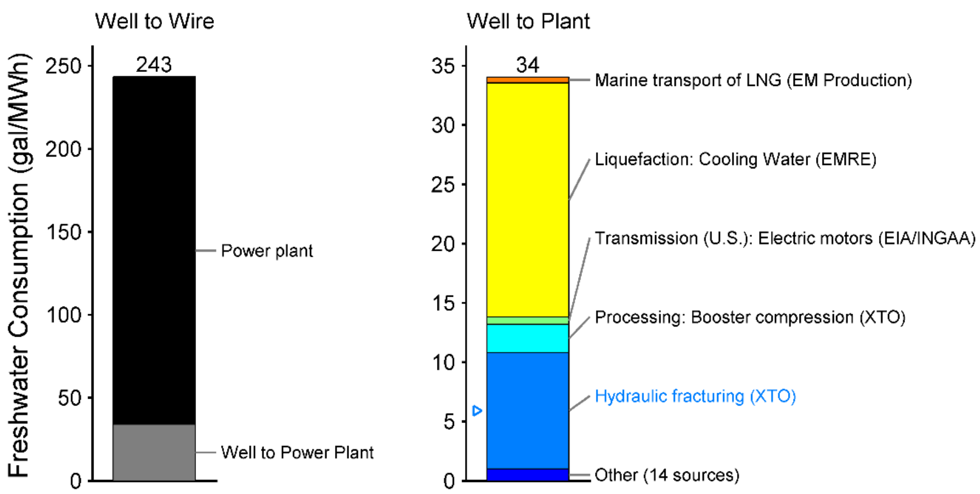


Figure 5. Breakdown of life cycle freshwater consumption associated with Marcellus Shale gas exported as LNG to Mumbai (India) for power generation. A complete list of technology and parameter assumptions is available in supporting information (SI, Table S13). The text parenthesis for each block in the well-to-plant freshwater consumption plot refers to the source of data used. EIA = U.S. Energy Information Administration, XTO = ExxonMobil subsidiary involved with production and processing of shale gas, EM = ExxonMobil, EMRE = ExxonMobil Research and Engineering.

We report the base case, life cycle freshwater consumption associated with Marcellus shale gas used as a fuel for power generation in India in Figure 5. As in domestic U.S. natural gas life cycles, evaporative freshwater losses associated with closed-loop cooling at the (CCGT) power plant constitute the largest source of freshwater consumption over the natural gas life cycle (86% of life cycle). All other operations collectively contribute approximately 14% of the life cycle freshwater consumption. The largest single freshwater consumer from "Well to Plant" is closed cooling towers associated with power generation equipment at the liquefaction facility, i.e. co-generation systems for steam and power (8% of life cycle). If once-through water cooling is used in lieu of closed loop evaporative cooling towers at the liquefaction facility, then life cycle freshwater consumption may be reduced to 224 gal/MWh (Figure S10). Freshwater consumed via hydraulic fracturing (9.9 gal H_2O/MWh) constitutes an additional 4%, and the majority of the remaining 2% is associated with grid electricity utilized to drive compressors associated with gas processing and transmission (3 gal/MWh). As discussed in Methods, we exclude the freshwater consumption associated with hydropower from the life cycle freshwater consumption associated with purchased electricity. Were we to include the impacts of purchased hydropower, the life cycle freshwater of Marcellus gas used for power generation outside of the U.S. would increase to 256 gal H_2O/MWh (see Figure S10), 16 gal/MWh of which would be associated with gas processing and transmission.

3.2. Variability and Uncertainty Analysis

As discussed in Methods, we conducted Monte Carlo simulations to assess the uncertainty of each Marcellus shale gas life cycle ending at a different country, thereby allowing a comparison of life cycle uncertainty to life cycle variability (i.e. by location of end use of the gas). Our results are illustrated in Figure 6. With the exception of the special case of the U.S., where gas is not transported as LNG, there is considerable overlap between the distributions of life cycle GHG emissions, reflecting the minor contributions of shipping related GHG emissions illustrated in Figure 4. Thus, we conclude that variability in GHG emissions (464 - 477 kg CO_2eq/MWh) among LNG pathways is negligible relative to uncertainty of those emissions (e.g. uncertainty range (10th to 90th percentile) for India 452 - 503 kg CO2eq/MWh). The life cycle GHG impact of power generated from Marcellus shale gas exported as LNG to various destinations range from 439 kg CO_2eq/MWh (10th percentile, Milford Haven, UK) to 503 kg CO_2eq/MWh (90th percentile, Yokohama, JP).

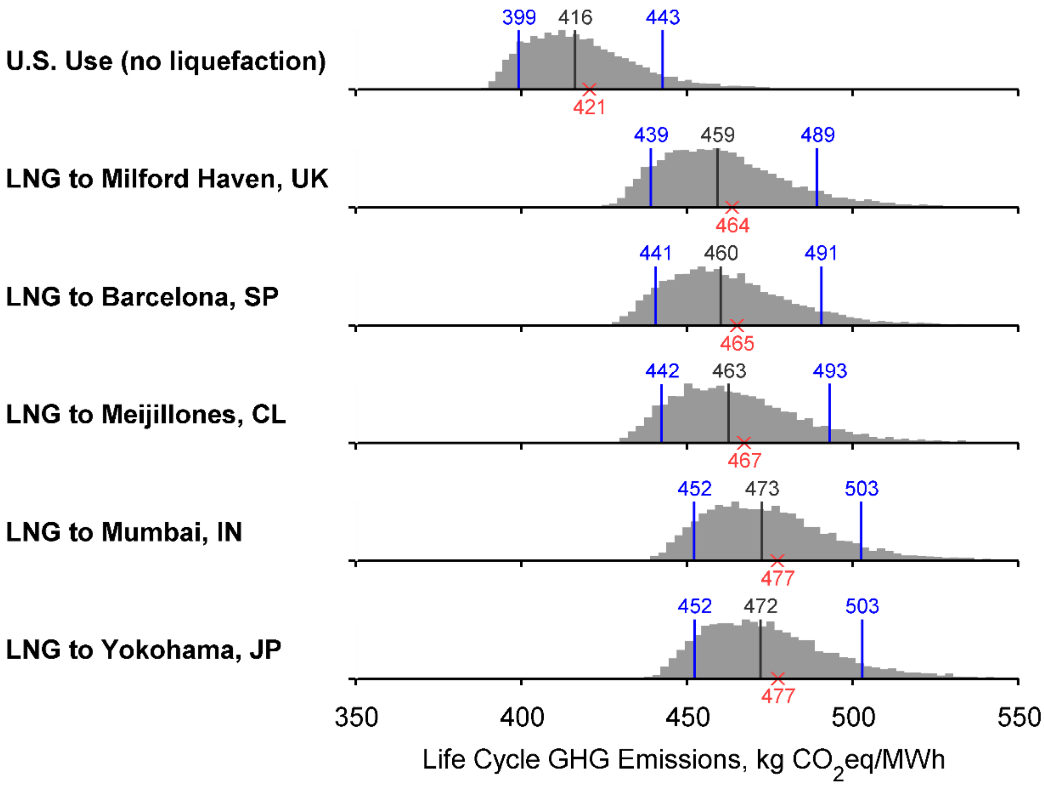


Figure 6. Distributions of life cycle GHG emissions of Marcellus shale gas use at a CCGT power plant at different destinations. GHG reported using IPCC AR5 GWPs (100-year). For each destination, the distributions were obtained using Monte Carlo simulations, where for each trial of the simulation (total trials =10000), realizations of input data (e.g. EUR, flowback gas volume and so on) were chosen at random from their underlying distribution. The blue bars represent the 10th and 90th percentile values of the resulting distribution, while the red "x" refer to the mean values.

3.3. Sensitivity analysis

To elucidate the drivers of the uncertainty in life cycle GHG emissions and assess the impact of technology choice in the life cycle of LNG, we conducted one-dimensional sensitivity analyses of the life cycle GHG emissions (Figure 7), fraction of gross methane noncombustively emitted over the life cycle (Figure S9), life cycle freshwater consumption (Figure S10), and LNG-plant-specific impacts and energy consumption (Figure S7). The results of the first of these investigations are reported in Figure 7, in which we have summarized the 15 data inputs and parameters that have the greatest impact on the life cycle GHG emissions associated with LNG use for power generation. The base case in all of these analyses was the life cycle of LNG from the Marcellus to an Indian CCGT power plant operating at 50.2% efficiency on an HHV basis (55.7% on an LHV basis), see Methods).

The key drivers for the breadth of the distributions reported in Figure 6 are the expected ultimate recoveries (EURs) of Marcellus wells, the utilization of compressor stations for transmission pipelines, and the fugitive emissions associated with gas gathering systems. The sensitivity of LCAs of shale gas to

EUR has been discussed by other studies ([3, 19, 20]). Increasing or decreasing the annual operating hours for various compressor stations impacts the total prime mover electrical consumption and fuel consumption for the entire U.S. gas transmission network, which correspondingly affects the life cycle GHG emissions. The data used here, corresponding to 2012 U.S. gas transmission network operations, suggests that the individual compressors were operated on average for 2806 hours per year or around 32% of the time (Figure S3). The distributions of fugitive CH_4 emissions from the gathering system, processing plant, and transmission system were adopted from the aforementioned EDF studies ([8, 9, 10]). Insofar as we adopted these distributions for the liquefaction and regasification stages as well, life cycle GHG emissions have equivalent sensitivities to these fugitives.

The life cycle GHG emissions were less sensitive to fugitive emissions and energy usage associated with regasification, raw gas type (rich vs lean), and gas treatment technology at the LNG plant owing to the relative contributions of regasification, processing and liquefaction to the life cycle GHG emissions (Figure 3). Similar considerations affect the sensitivity of the life cycle GHG emissions to fugitive CH_4 emissions from the gathering system equipment (chemical injection pumps, pneumatics, etc. [8]) and the well lifetime.

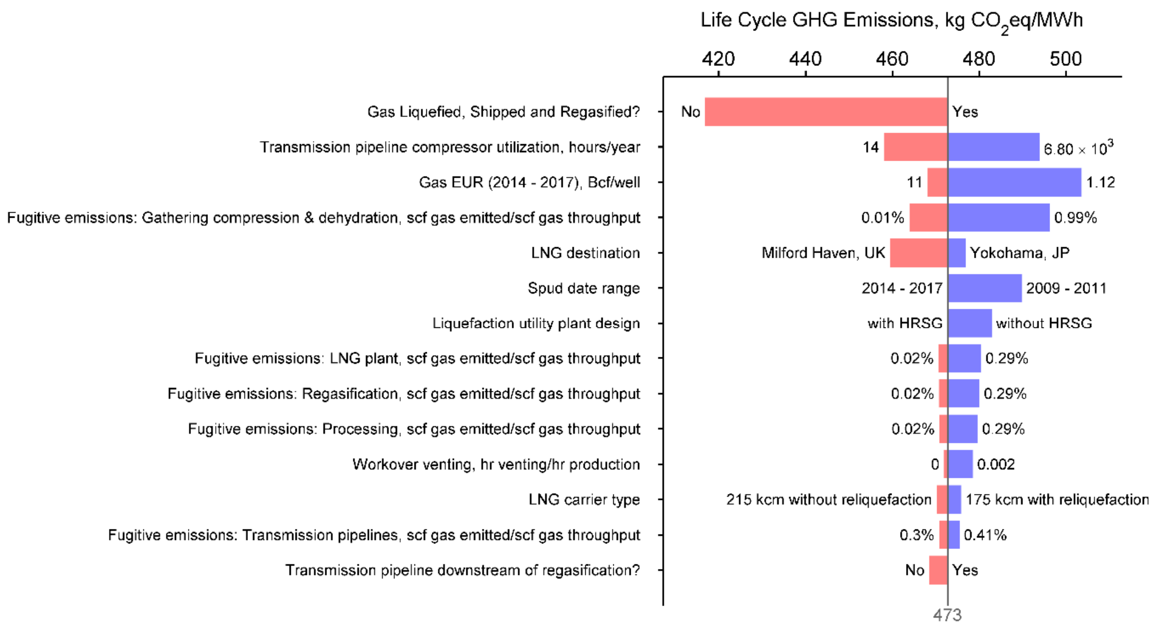


Figure 7. Sensitivity of fife cycle GHG emissions to input data and parameters (Tornado diagram). GHG reported using IPCC AR5 GWPs (100-year). Tornado results were calculated by systematically varying each data set to the 5th or 95th percentile value of its input distribution. For parameters, Tornado results were estimated by varying across all possible parameter values. For example, the parameter LNG destination considers destinations of United Kingdom, Japan, Chile, Spain and India. kcm = 100,000 m^3. HRSG = Heat Recovery Steam Generator.

Figure 7 also illustrates the effects of technology and decisions upon the life cycle GHG emissions not captured by Monte Carlo simulation, i.e. effects of life cycle variability. As previously discussed, the results of the LCA are particularly sensitive to the presence or absence of operations associated with LNG (relative to U.S. end use of gas) and the destination of LNG. They are also sensitive to technology choice to varying degrees. For instance, operating an LNG plant without co-generation may increase life cycle GHG emissions by 2%, but transporting LNG in a ship that does not feature reliquefaction may reduce life cycle GHG emissions by 0.5%.

These sensitivities are consequences of energy efficiency. At the liquefaction plant (Figure S6), a heat recovery steam generator (HRSG) generated steam from hot exhaust gases exiting the (liquefaction) gas turbines providing mechanical power to the refrigeration compressors enabling the liquefaction. This in turn (1) reduces the fuel gas requirement for generating process steam and electrical power, and (2) allows the facility to produce excess electricity (currently up to 49.9 MW) that may be exported to the grid. In our LCA, grid exports were calculated as a GHG credit using the approach employed in LCAs of biofuels, oil sands, and other products manufactured with co-generation, i.e. displacement of an equivalent amount of grid electricity (Table S12). Hence, employing a HRSG system at the liquefaction facility reduces life cycle GHG emissions by 2%.

Similar considerations drive the sensitivity to shipping: life cycle GHG emissions are higher for Asian destinations relative to European destinations due to distance, and thus ship fuel consumption. Moreover, ships with larger LNG storage capacities (215,000 m^3) have lower fuel consumption per unit of cargo compared to smaller ships (175,000 m^3) for the same shipping distance. Lastly, the ability to re-liquefy gas on board and thereby deliver more LNG at the destination is more than offset by the energy consumption – and concomitant GHG emissions, associated with on-board re-liquefaction. The choice of adsorption or cryogenic distillation for HHC removal at the liquefaction facility, although less important than the presence or absence of a HRSG system, also appears in the top 20 most sensitive variables impacting the life cycle GHG emissions. Adsorption technologies selectively remove heavy components in the gas feed (C_6+) and predominantly use heat (at 250-300 ^oC) for regenerating the adsorption bed (SI technical descriptions for SeparSIV and mole sieves). By contrast, cryogenic distillation consumes electricity as the predominant energy input, and removes lighter (C_3+) components of the gas feed along with heavy hydrocarbons. The net result of using adsorption over cryogenic distillation for HHC removal is a 7% reduction in the GHG emissions associated with a U.S.-based facility that liquefied pipeline-quality gas (Figure S7).

As part of this sensitivity analysis, we also considered the effect of the changes in upstream practices in the Marcellus in recent years. Replacing the EURs, fuel usage for drilling and completion, and other upstream operating data reported in the SI with operating data from 2009 – 2011 reported by Laurenzi and Jersey (2013) results in an increase in life cycle GHG emissions of 3.6%, i.e. life cycle GHG emissions of Marcellus wells drilled from 2014 through 2017 are about 3.6% lower than those drilled from 2009 – 2011. There are a few key reasons for this: EURs have increased almost threefold, thereby decreasing the normalized emissions associated with drilling and completion (Figure S1), flaring associated with flowback gas following hydraulic fracturing has decreased by over 97% on average (Figure S1), as reduced-emission completions ("green completions") have replaced flaring, and advances in drilling and hydraulic fracturing practices have reduced the fuel requirements per volume of gas recovered from shale gas wells.

3.4.Comparison with Prior Work

As we show in Table S14, there are noteworthy differences between the findings of this study and prior LCAs of U.S. LNG sourced from shale gas. In the course of our study, we identified some, but not all of the reasons for these discrepancies.

The most notable cause of the differences is the selected CCGT power plant efficiency: two studies [15, 14] employed an efficiency of 46% (HHV basis), which is reflective of the average fleet-wide U.S. CCGT efficiency in 2015. By contrast, our study uses a 50.2% efficiency (HHV basis), which is typical of a new CCGT plant and the predominant efficiency used in LCAs of natural gas power ([21, 5, 22, 23, 24]).

A second cause of the discrepancies is the amount of methane non-combustively emitted over the Marcellus life cycle as a fraction of gross gas production, also referred as the “fugitive CH_4 leakage rate”. Abrahams and coworkers adopted a value of 3% for their study [15]) whereas we estimate it to be 1.2% via bottom-up integration of the findings of the EDF studies of methane fugitives (Table S14, [8, 10, 9]).

Our estimate of the GHG emissions associated with liquefaction differs substantially from those of both the Abrahams and NETL studies NETL employed an estimate of 8.5 g CO_2eq/MJ of LNG (LHV basis), whereas Abrahams and coworkers adopted a base case estimate of 6.9 gCO_2eq/MJ of LNG (LHV basis) (Table S14). These estimates are 2 – 3 times higher than our engineering-based estimate for a U.S. facility that takes pipeline quality gas as a feed (2.7 g CO_2eq/MJ LHV, Figure S7). The discrepancy is almost certainly due to the fact that both Abrahams and coworkers and NETL have relied on secondary data sources or secondary estimates for GHG emissions associated with liquefaction. These estimates would have been for large scale LNG plants of varying ages, which process raw gas from the field instead of pipeline gas. As a consequence, such facilities include the operations within the processing phase of the U.S. gas life cycle and possibly additional operations including NGL fractionation. They would also be affected by the location of the historical LNG facilities, likely cover a range of feed gas compositions (e.g. more or less heavy hydrocarbons, impurities like H_2S and CO_2), power generation choices, and liquefaction facility designs in different regions. Even changes in ambient temperature assumptions have a considerable impact on the mechanical power consumed by the refrigeration cycle for liquefaction and consequently the facility GHG emissions [25]. Hence, using secondary sources in analyzing LCA of U.S. LNG exports cannot accurately account for the technological uniqueness of U.S. LNG plants, which are fed by pipeline-quality gas. In contrast, the U.S. liquefaction facility modeled in our study accounts for, among other things: 1) the relatively low impurity (e.g. H_2S) concentrations in the feed gas sourced from the pipeline network and 2) use or absence of heat recovery steam generators (HRSG) to recover energy from the gas turbine exhaust. The use of turbine exhaust heat to either raise steam for electricity or supply process heat is part of the design for at least five liquefaction terminals under construction in the U.S. Gulf Coast [26, 27, 28, 29] and East Coast [30]. Use of combined heat and power design is estimated to result in 33% lower facility GHG emissions compared to a design that does not recover waste heat from the gas turbines exhaust (Figure S7). Finally, the share of life cycle GHG emissions attributed to the regasification stage is notably higher (3%) for one of the studies compared to the values estimated here and by other literature reports [15, 31] (Table S14). We have provided additional comparisons between the findings of our study and those in the literature are presented in SI Section S9.

4. Conclusions

Using the most up to date field data from Marcellus operations, experimentally-determined estimates of fugitive methane emissions from natural gas operations, and engineering data and tools for the design of LNG plants, we estimate the typical life cycle GHG emissions of Marcellus shale gas exported as LNG to different destinations in Asia, Europe and Latin America to be between 459 kg CO_2eq/MWh and 473 kg CO_2eq/MWh, depending on the destination. The three most important factors impacting the life cycle GHG emissions to be the power requirement for gas transmission (vis-à-vis compressor utilization), the ultimate recovery of the well and fugitive CH_4 emissions associated with gathering system operations in the production stage of the gas life cycle. Indeed, the increase in EURs of wells drilled in the Marcellus region since 2009 and adoption of "green completions" have reduced life cycle GHG emissions of Marcellus gas.

Within the LNG supply chain, the adoption of waste heat recovery at the liquefaction facility offers the greatest potential to reduce GHG emissions, although it comes at a cost of freshwater consumption if closed-loop cooling is employed. Moreover, the employment of adsorption-based technologies to remove residual levels of pentanes and larger molecules from pipeline-quality gas has the potential to reduce facility-level GHG emissions by 7% relative to cryogenic separation. These findings highlight the importance of bottom-up process modeling in life cycle assessment, which facilitates context-specific investigation of environmental impacts at the process level. This, in turn may help engineers select "greener" options throughout the design process and weigh tradeoffs among environmental indicators. By contrast, generic "inventories" of emissions and/or energy usage for liquefaction may be highly specific to the facilities from which they were modeled. To wit, we find that peer-reviewed LCAs of LNG published in recent years have overestimated GHG emissions from liquefaction insofar as they adopted data from non-U.S. facilities featuring technology that would not be present in a U.S. facility. U.S. LNG facilities are unique in that they process pipeline quality gas, which has substantially lower levels of CO_2, water, light hydrocarbons and other molecules present in the "raw" natural gas streams that feed LNG plants elsewhere in the world. Ultimately, we find when used for power generation outside of the U.S. – i.e. when exported as LNG, the life cycle GHG emissions of Marcellus shale gas increase by 10 – 13% depending upon the destination.

The "bottom up" approach to life cycle assessment also facilitated our use of the latest measurements of fugitive CH_4 emissions across the U.S. natural gas supply chain to yield a life cycle fugitive CH_4 leakage rate for the base case destination of Mumbai, India to be 1.2% (80% CI: 0.80-1.80%). As previously mentioned, this is due in part to the increase in EUR, which is the denominator of this fraction, but it is also due to the use of a single pneumatic device per well at Marcellus well pads.

The results of our analysis may be used to inform comparisons of the environmental impacts of LNG-based power generation and competing power generation options (e.g. coal) relevant to each destination country, provided that the comparison is to be made between "new build" power generation facilities. However, if "fleet wide" LCAs are desired, i.e. the end use phase of the gas life cycle is to be representative of existing power plants in a given country, then additional country-specific data would be required, including for the heat rates of the CCGT power plants in the country of interest and country specific data regarding gas transmission infrastructure downstream of the regasification plant. Furthermore, we have employed a power generation efficiency of 55.7% (LHV basis, equivalent to 50.2% on HHV basis), which corresponds to a facility with one or more F-class turbines and HRSGs. If fuel-cell-based power plants [32] or newer H-class turbines are employed for new power plant projects, then the efficiencies of these facilities may exceed 60% on an LHV basis (i.e. the GE 9HA [33] or Siemens SGT5-800H [34]), leading to reduced life cycle impacts (per MWh of generated electricity) of the resulting gas power.

Acknowledgements

We thank Owen Hehmeyer, Michael O'Connor, John McMichael, and Adam Bymaster of XTO Energy, Scott Northrop of ExxonMobil Upstream Research Company, Jeff Matthews of H2W United LLC, and Julie Gruhn, Trevor Smith, Denise Voelker, Meredith Winczewski, and Edward Zbacnik of Honeywell UOP for providing subject matter expertise and technical data used in this study. We also thank Dan Zimmerle of Colorado State University for helpful conversations about fugitive transmissions associated with gas transmission.

References

[1] Energy Information Administration, "Annual Energy Outlook 2016: with projections to 2040," U.S. Energy Information Administration, Washington, DC, 2016.

[2] G. A. Heath , P. O'Donoughue, J. D. Arent and M. Bazilian, "Harmonization of initial estimates of shale gas life cycle greenhouse gas emissions for electric power generation," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 111, no. 31, pp. E3167-E3176, 2014.

[3] I. J. Laurenzi and G. R. Jersey, "Life cycle greenhouse gas emissions and freshwater consumption of Marcellus shale gas," *Environmental Science & Technology,* vol. 47, no. 9, pp. 4896-4903, 2013.

[4] A. Burnham, J. Han, C. E. Clark, M. Wang, J. B. Dunn and I. Palou-Rivera, "Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and Petroleum," *Environmental Science & Technology,* vol. 46, no. 2, pp. 619-627, 2012.

[5] M. Jiang, M. W. Griffin, C. Hendrickson, P. Jaramillo, J. VanBriesen and A. Venkatesh, "Life cycle greenhouse gas emissions of Marcellus shale gas," *Environmental Research Letters,* vol. 6, no. 3, p. 034014, 2011.

[6] A. T. Dale, V. Khanna, R. D. Vidic and M. M. Bilec, "Process Based Life-Cycle Assessment of Natural Gas from the Marcellus Shale," *Environmental Science & Technology,* vol. 47, no. 10, pp. 5459-5466, 2013.

[7] National Energy Technology Laboratory, "Life Cycle Analysis of Natural Gas Extraction and Power generation," National Energy Technology Laboratory, Pittsburgh, PA, 2016.

[8] D. T. Allen, M. V. Torres, J. Thomas, D. W. Sullivan, M. Harrison, A. Hendler, S. C. Herndon, C. E. Kolb, M. P. Fraser, D. Hill, B. Lamb, J. Miskimins, R. F. Sawyer and J. H. Seinfeld, "Measurements of methane emissions at natural gas production sites in the United States," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 110, no. 44, pp. 17768-17773, 2013.

[9] A. L. Mitchell, D. S. Tkacik, J. R. Roscioli, S. C. Herndon, T. I. Yacovitch, D. M. Martinez, T. L. Vaughn, L. L. Williams, M. R. Sullivan, C. Floerchinger, M. Omara, R. Subramanian, D. Zimmerle, A. Marchese and A. L. Robinson, "Measurements of Methane Emissions from Natural Gas Gathering Facilities and Processing Plants: Measurement Results," *Environmental Science & Technology,* vol. 49, no. 5, pp. 3219-3227, 2015.

[10] D. J. Zimmerle, L. L. Williams, T. L. Vaughn, C. Quinn, R. Subramanian, G. P. Duggan, B. Wilson, J. D. Opsomer, A. J. Marchese, D. M. Martinez and A. L. Robinson, "Methane Emissions from the Natural Gas Transmission and Storage System in the United States," *Environmental Science & Technology,* vol. 49, no. 15, pp. 9374-9383, 2015.

[11] R. A. Alvarez, S. W. Pacala, J. J. Winebrake, W. L. Chameides and S. P. Hamburg, "Greater focus needed on methane leakage from natural gas infrastructure," *Proc. Natl. Acad. Sci. USA,* vol. 109, no. 17, pp. 6435-6440, 2012.

[12] N. N. Clark, D. L. McKacin, D. R. Johnson, S. W. Wayne, H. Li, V. Akkerman, C. Sandoval, A. N. Covington, R. A. Mongold, J. T. Hailer and O. J. Ugarte, "Pump-to-Wheels Methane Emissions from the Heavy-Duty Transportation Sector," *Environmental Science & Technology,* vol. 51, no. 2, pp. 968-976, 2017.

[13] F. Tong, P. Jaramillo and I. M. L. Azevedo, "Comparison of Life Cycle Greenhouse Gases from Natural Gas Pathways for Light-Duty Vehicles," *Env. Sci. Technol.,* vol. 29, no. 9, pp. 6008-6018, 2015.

[14] National Energy Technology Laboratory, "Life Cycle Greenhouse Gas Perspective on Exporting Liquefied Natural Gas from the United States," National Energy Technology Laboratory, Pittsburgh, PA, 2014.

[15] L. S. Abrahams, C. Samaras, M. Griffin and S. Matthews, "Life Cycle Greenhouse Gas Emissions From U.S. Liquefied Natural Gas Exports: Implications for End Uses," *Environmental Science &*

Technology, vol. 49, no. 5, pp. 3237-3245, 2015.

[16] R. Raj, S. Ghandehariun, A. Kumar and M. Linwei, "A well-to-wire life cycle assessment of Canadian shale gas for electricity generation in China," *Energy,* vol. 111, pp. 642-652, 2016.

[17] International Gas Union, "2016 World LNG Report," International Gas Union, 2016.

[18] G. Myhre, D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura and H. Zhang, "Anthropogenic and Natural Radiative Forcing," in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge, UK, Cambridge University Press, 2013.

[19] T. Stephenson, J. E. Valle and X. Riera-Palou, "Modeling the Relative GHG Emissions of Conventional and Shale Gas Production," *Environmental Science & Technology,* vol. 45, no. 24, pp. 10767-10764, 2011.

[20] A. Burnham, J. Han, C. E. Clark, M. Wang, J. B. Dunn and I. Palou-Rivera, "Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and Petroleum," *Environmental Science & Technology,* vol. 46, no. 2, pp. 619-627, 2012.

[21] National Energy Technology Laboratory, "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity," National Energy Technology Laboratory, Pittsburgh, PA, 2010.

[22] A. Venkatesh, P. Jaramillo, W. M. Griffin and H. S. Matthews, "Uncertainty in Life Cycle Greenhouse Gas Emissions from United States Natural Gas End-Uses and its Effects on Policy," *Environmental Science & Technology,* vol. 45, no. 19, pp. 8182-8189, 2011.

[23] P. Jaramillo, W. M. Griffin and H. S. Matthews, "Comparative Life-Cycle Air Emissions of Coal, Domestic Natural Gas, LNG, and SNG for Electricity Generation," *Environmental Science & Technology,* vol. 41, no. 17, pp. 6290-6296, 2007.

[24] J. Coleman, A. S. Kasumu, J. Liendo, V. Li and S. M. Jordaan, "Calibrating Liquefied Natural Gas Export Life Cycle Assessment: Accounting for Legal Boundaries and Post-Export Markets," Canadian Institute of Resources Law, Calgary, Canada, 2015.

[25] Air Products and Chemicals, Inc., "Arctic LNG Plant Design: Taking Advantage of the Cold Climate," Air Products and Chemicals, Inc., [Online]. Available: http://www.airproducts.com/~/media/files/pdf/industries/lng/arctic-lng-plant-design.pdf. [Accessed 12 June 2017].

[26] Federal Energy Regulatory Commission, "Golden Pass LNG Export Project: Final Environmental Impact Statement," Federal Energy Regulatory Commission (FERC), Washington, DC, 2016.

[27] Federal Energy Regulatory Commission, "Magnolia LNG and Lake Charles Expansion Project: Final Environmental Impact Statement," Federal Energy Regulatory Commission (FERC), Washington, DC, 2015.

[28] Federal Regulatory Energy Commission, "Environmental Assessment for the Sabine Pass Liquefaction Project," Federal Energy Regulatory Commission (FERC), Washington, DC, 2011.

[29] Federal Energy Regulatory Commission, "Freeport LNG Liquefaction Project Phase II Modification Project: Final Environmental Impact Statement," Federal Energy Regulatory Commission (FERC), Washington, DC, 2014.

[30] Federal Energy Regulatory Commission, "Environmental Assessment for the Cove Point Liquefaction Project," Federal Energy Regulatory Commission (FERC), Washington, DC, 2014.

[31] P. Balcombe, K. Anderson, J. Speirs, N. Brandon and A. Hawkes, "The Natural Gas Supply Chain: The Importance of Methane and Carbon Dioxide Emissions," *ACS Sustainable Chemistry & Engineering,* vol. 5, pp. 3-20, 2017.

[32] FuelCell Energy, "SureSource 4000 - 3.7 MW," 26 January 2018. [Online]. Available: https://www.fuelcellenergy.com/wp-content/uploads/2013/11/Product-Spec-SureSource-4000.pdf. [Accessed 26 January 2018].

[33] GE Power, "9HA Power Plants," 26 January 2018. [Online]. Available: https://www.gepower.com/content/dam/gepower-pgdp/global/en_US/documents/product/gas%20turbines/Fact%20Sheet/2017-prod-specs/9ha-power-plants.pdf. [Accessed 26 January 2018].

[34] Siemens, "SGT5-8000H heavy-duty gas turbine (50 Hz)," 26 January 2018. [Online]. Available: https://www.siemens.com/global/en/home/products/energy/power-generation/gas-turbines/sgt5-8000h.html#!/. [Accessed 26 January 2018].

[35] UNFCCC, "The Kyoto Protocol to the United Nations Convention on Climate Change," United Nations, New York, 1997.

[36] J. M. Kinkenbijl, M. L. Dillon and E. C. Heyman, "Gas Pre-Treatment and their Impact on Liquefaction Processes," in *GPA Nashville TE meeting*, Nashville, TN, 1999.

[37] A. Eastwood, "ProSteam—A Structured Approach To Steam System Improvement," *Energy Engineering,* vol. 100, pp. 59-79, 2003.

[38] UOP, "UOP SeparSIV Systems for Lean Natural Gas Processing," UOP LLC, A Honeywell Company, Des Plaines, IL, 2014.

[39] MAN, "ME-GI Dual Fuel MAN B&W Engines A Technical, Operational and Cost-effective Solution for Ships Fuelled by Gas," 26 January 2018. [Online]. Available: http://marine.mandieselturbo.com/docs/librariesprovider6/technical-papers/me-gi-dual-fuel-man-b-amp-w-engines433833f0bf5969569b45ff0400499204.pdf?sfvrsn=18%20downloaded%20Jan%208%202017. [Accessed 26 January 2018].

[40] A. Carlesimo, "The Adriatic LNG Terminal: Industrial Firsts into a fully operation reality," in *LNG 17 International Conference & Exhibition on Liquefied Natural Gas*, Houston, TX, 2013.

[41] ThinkStep, "Greenhouse Gas Intensity from Natural Gas," ThinkStep, 2017.

[42] National Energy Technology Laboratory, "Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3," National Energy Technology Laboratory, Pittsburgh, PA, 2015.

[43] M. Jiang, W. M. Griffin, C. Hendrickson, P. Jaramillo and J. VanBriesen, "Life cycle greenhouse gas emissions of Marcellus shale gas," *Environmental Research Letters,* vol. 6, p. 034014, 2011.

[44] National Renewable Energy Laboratory, "A Review of Operational Water Consumption and Withdrawal Factors for Electricity Generating Technologies," National Renewable Energy Laboratory, Golden, CO, 2011.

[45] A. Safaei, F. Freire and C. H. Antunes, "Life-Cycle Greenhouse Gas Assessment of Nigerian Liquefied Natural Gas Addressing Uncertainty," *Environmental Science & Technology,* vol. 49, pp. 3949-3957, 2015.

[46] W. Choi and H. Song, "Well-to-wheel analysis on greenhouse gas emission and energy use with natural gas in Korea," *International Journal of Life Cycle Assessment,* vol. 19, pp. 850-860, 2014.

[47] P. Barnett, *Life Cycle Assessment (LCA) of Liquefied Natural Gas (LNG) and its environmental impact as a low carbon energy source,* Toowoomba: University of Southern Queensland, 2010.

[48] Linde, "Natural Gas Liquids Recovery: CRYO-PLUS Technology," Linde Process Plants, Inc., Tulsa, OK, 2013.

[49] M. Anderson, K. Salo and E. Fridell, "Particle- and Gaseous Emissions from an LNG Powered Ship," vol. 49, no. 20, pp. 12568-12575, 2015.