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Reduction of greenhouse gas and criteria pollutant emissions by direct conversion of associated flare gas to synthetic fuels at oil wellheads

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Abstract

This study describes the results of a "well-to-wheel" life cycle assessment (LCA) carried out to determine the potential greenhouse gas and criteria pollutant emission reductions that could be achieved by converting associated flare gas directly to synthetic fuels at oil wellheads in the US and globally. A Greyrock Flare Gas-to-Fuels™ conversion process at an Ohio oil well was used as the base case for this LCA. The liquid fuel produced directly from associated gas is comprised primarily of premium synthetic diesel with a small amount of synthetic gasoline. In this LCA scenario, the synthetic diesel and synthetic gasoline are blended at 20 and 10 vol% with petroleum diesel and gasoline, respectively. While the synthetic diesel fuel can be used as is (100%), the 20 vol% synthetic diesel blend (with petroleum diesel) was found to significantly improve engine performance, increase fuel economy, and reduce emissions. The direct conversion of associated gas to synthetic diesel fuels globally could reduce emissions of CO_2 and CH_4 by up to 356 and 5.96 million metric tons/year, respectively, resulting in the reduction of greenhouse gases (GHGs) by about 113.3 and 92.2% (20 year global warming potential) and 73.8 and 50.7% (100 year global warming potential) for synthetic diesel and gasoline fuels when compared to petroleum-derived gasoline fuels, respectively. Likewise, diesel criteria emissions could be reduced globally by up to 23.3, 0.374, 42.4, and 61.3 million metric tons/year globally for CO, particulates, NOx, and hydrocarbons, respectively. The potential economic benefit of this approach is that up to 5.30 and 71.1 billion liters of synthetic fuels could be produced each year in the US and globally from associated gas, respectively.

Keywords Associated flare gas · Direct synthetic fuel production · Flare emissions · Vehicle emissions · Greenhouse gas emissions · Criteria pollutant emissions · Well-to-wheel life cycle assessments (WTW-LCA) · Economic benefits

Introduction

Natural gas was first used by the Chinese in about 900 B.C.E. to evaporate seawater for salt production. By the first century, the Chinese had developed more advanced techniques for tapping underground reservoirs of natural gas, which allowed them to drill wells as deep as 1460 m. They used metal drilling bits inserted through sections of hollowed-out bamboo pipes to reach the gas and bring it to the surface [1].

In 1859, George Bissell and Edwin L. Drake made the first successful use of a boring rig on a well drilled principally to produce oil, at a site on Oil Creek near Titusville, Pennsylvania. At that time, Bissell and Drake found that large volumes of natural gas (NG) were co-produced when the crude oil was extracted from the ground. This NG has come to be commonly referred to as associated gas which is primarily comprised of methane with minor concentrations of C_2–C_6 hydrocarbons, nitrogen, and some trace gases such as SO_2. Since the collection and aggregation of this associated gas for commercial consumption require costly investment, such as pipelines which costs an average of $4.10 million/km during 2014 in the US [2], this gas is usually burned or flared. This combusted-associated gas is typically referred to as flare gas.

Another problem is that many wells are often drilled over a large area during a short period of time, because oil production is subjected to a high depletion rate [3]. Therefore, planning the appropriate infrastructure is challenging for the commercialization of associated gas. As a result,

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approximately 11.2 and 150 billion cubic meters (bcm) of associated gas are flared in the US and globally each year [4–6], respectively, with no energy or commercial benefit. To put this in perspective, if this 150 bcm of gas was converted into power, it could provide more than enough electricity to supply the entire African continent each year.

The composition of associated gas varies depending upon the location of the oil well. Different sources have varying concentrations of CH_4, gas-phase hydrocarbons (C_2–C_5), condensate (C_5 + hydrocarbons), CO_2, inert gases (N_2, Ar, He), and contaminants such as H_2S. Table 1 summarizes some of these differences for a typical oil well in Ohio [7], oil wells in China [8], a characteristic well in Texas, and other wells outside of the US [9]. The gas composition for the Ohio well was used as the base case for this LCA study. CH_4, CO_2, and the other gases, listed in Table 1, are separated from the crude oil before the oil is piped or transported to refineries. Since there is no market for this associated gas, it is often combusted in flares at the oil production site.

Although CH_4 and CO_2 are the primary greenhouse gases present in associated gas emissions, N_2O is another potentially potent greenhouse gas, but there are no reliable measurements of N_2O emissions from associated gas flares at this time. Therefore, N_2O emissions were not included in this study.

Because all global warming potentials (GWPs) are calculated relative to CO_2, GWPs based on a shorter timeframe are larger for gases with shorter lifetimes than that of CO_2. For example, CH_4, which has a relatively short lifetime compared to CO_2, the 100-year GWP of 28–36 is much less than the 20-year GWP of 84–87 [10].

Although the International Panel on Climate Change (IPCC) working group typically has used a 100 years in GHG modeling [11, 12], the modeling in this paper is focused on a 20-year GWP of 84, since recent models predict significant increases in atmospheric CH_4 and CO_2 concentrations with concomitant increases in global temperatures are expected to occur during the next 15–25 years [13, 14]. In addition, the average lifetime of an oil well is about 20 years. Nevertheless, the 100-year GWP was also determined for comparison purposes.

Benzene, formaldehyde, polycyclic aromatic hydrocarbons (PAHs), NOx, SO_2, acetaldehyde, and acrolein are also emitted from flaring of the associated gas [15–17] in addition to the criteria pollutants and greenhouse gases. It has been estimated that the annual emissions (GHG and non-GHG) from these flares are about the same as the yearly emissions from 70 million cars or about 120 average sized US coal-fired power plants [18].

The "Zero Routine Flaring by 2030" initiative introduced by the World Bank is supported by governments, oil and gas companies, universities, and institutes who have recognized that associated gas flaring is unsustainable from both economic and environmental perspectives. Therefore, these global organizations have agreed to collaborate with the objective of significantly reducing routine-associated gas flaring by 2030 [19, 20]. However, regulations on gas flaring are set at national and sub-national levels, and therefore, there is wide variation regarding the permissibility of flaring, conditions under which flaring is allowed, and reporting requirements.

In 2018, Elvidge et al. [21] compared 2015 satellite-derived gas flaring data with greenhouse gas reduction targets. It was found that Russia and the US could only meet a small portion ($< 2.5\%$) of their gas flaring reduction targets by 2017. They concluded that this was in part due to the absence of regulations on gas flaring and the lack

Table 1 Average associated flare gas composition from oil wells at several global locations

Well locations	Ohio (base case well)	Texas wells	Netherland wells	China wells	Saudi Arabia wells	Indonesia wells
Constituent	Concentration (vol%)					
Methane (CH_4)	87.9	85.4	81.3	93.9	56	65.7
Ethane (C_2H_6)	5.6	11	2.9	0.72	18	8.5
Propane (C_3H_8)	2.1	2.9	0.4	0.08	9.8	14.5
Butane (C_4H_{10})	1.0	nd	0.1	0.02	4.5	5.1
Pentane (C_5H_{12})	0.3	nd	0.1	0.01	1.6	0.8
Carbon dioxide (CO_2)	0.5	0.4	0.9	4.6	8.9	4.1
Oxygen (O_2)	nd	nd	nd	nd	nd	nd
Nitrogen (N_2)	2.5	0.3	14.3	0.6	1.2	1.3
Hydrogen sulfide (H_2S)	0.007	nd	nd	0.057	nd	nd
Helium (He)	0.12	nd	nd	nd	nd	nd
Total	100.0	100.0	100.0	100.0	100.0	100.0

nd not determined

of reliable and cost-effective technologies for the conversion of flare gas to fuels and/or chemicals at the wellhead.

The World Bank carried out an evaluation of distributed technologies that had the potential capability of monetizing flare gas by converting it into valuable drop-in fuels and/or chemicals [19]. Greyrock Energy [22–25] and Oberon Fuels [26] were chosen as the global technology leaders in terms of overall low risk and shortest time to commercialization. Greyrock produces synthetic diesel and synthetic gasoline fuels which are ready to use "drop-in" fuels, whereas Oberon produces dimethyl ether which is a potential, future clean fuel for diesels.

In 2016, there were about 7500 major gas flares globally that emitted about 150 bcm of associated gas and recent data indicates that global gas flaring may be increasing [20]. However, our study assumes that the number and volume of gas flares will remain relatively constant during the next 20 years which is the time frame for this study.

Although several LCA studies have been carried out to determine the emissions of greenhouse gas emissions produced from natural gas production [27–30], no work has been carried out to quantify the potential reduction in greenhouse gas and criteria pollutant emissions by direct conversion of associated flare gas to synthetic fuels at the oil wellhead and the use of that fuel regionally. Therefore, the objective of this work was to carry out a comprehensive WTW-LCA to quantify the potential reduction in greenhouse gases and criteria pollutant emissions from associated gas flared at a representative well in Ohio, in the US, and globally, the production of synthetic liquid fuels from the associated gas at the wellhead and the local use of those synthetic fuels in on-the-road vehicles.

Approach

The database for the WTW-LCA was established by quantifying the potential reduction in greenhouse gas and criteria pollutant emissions for the representative associated gas flare in Ohio and existing flares in the US and globally by quantifying:

1. The reduction in flare gas emissions (g/MJ) when the associated gas is no longer flared but converted directly to synthetic liquid fuels at the oil wellhead.
2. The fugitive emissions of associated flare gas at the wellhead during oil production which includes CH_4 and CO_2 emissions (g/MJ) from oil drilling, collection of the associated gas, and transfer to the co-located synthetic fuel production plant.

3. The emissions (g/MJ) produced from the flare to fuel production plant.
4. The average reduction in diesel emissions (g/MJ) for synthetic diesel fuels compared to petroleum diesel fuels for 1996–2016 model-year diesel vehicles.

These reductions were first quantified for the Ohio oil well that produces an average of 8.47×10^6 m^3 of associated gas each year. In comparison, oil wells in the US and globally produces an average of 11.17×10^9 and 150 m^3 of associated gas each year, respectively. Using the assumption that other flares in the US and globally had basically the same average associated gas composition as the Ohio well, then the emission reductions for the US and globally was then determined by multiplying the GHG and criteria pollutant emissions from the Ohio well case by 1319 and 17,710, respectively.

Associated gas flares

The total volume of associated flare gas in the US has been determined using a US National Oceanic and Atmospheric Administration (NOAA) remote-sensing satellite. It was estimated that the total associated natural gas production during 2012 was 7.10 bcm from the production of 2.06 billion barrels of oil which amounted to 3.45 m^3 of associated gas produced per barrel of oil [31]. This relationship was used to estimate the total associated gas produced during 2016. Since the US crude oil production during 2016 was 3.24 billion barrels [32], it was estimated that the total associated natural gas production in the US during 2016 was about 11.17 bcm (see Table 2).

The transmission and storage leakage rate of the associated gas is a function of transmission distance and is scaled by the distance in the GREET model [33]. Associated gas from the wellheads is unprocessed before flaring. In a few cases, associated gas may be combined from several wells that are within an 8 km radius. However, the example used for this LCA is the direct conversion of flare gas to fuels at the base case wellhead located in Ohio. Therefore, the transmission distance for this associated gas was 0.0 km.

The LCA model used unprocessed associated flare gas at the wellheads as the feedstock for fuel production. As illustrated previously in Table 1, the type, depth, and location of the underground associated gas deposit and the geology of the area dictate the gas composition. Since the associated gas from the wellhead was not processed, any GHG emissions typically associated with gas processing were not included in the LCA models.

Associated gas emissions from oil wellheads are generated from venting (e.g., leaks) and flaring. Venting and leaks

Table 2 Associated flare gas produced with US crude oil during 2016

Product	g/MJ[a,b,c]	Total production/year
Crude oil[a,b]	26.0	3.24 billion barrels
		477.3 billion liters
		1.88×10^{13} MJ
		5.15×10^{14} g hydrocarbons
Associated gas[c]	21.1	11.17 bcm
		4.53×10^{11} MJ
		0.086×10^{14} g hydrocarbons

[a]The average energy content of one barrel of US oil is 6120 MJ

[b]The average mass for one barrel of US oil is 158,987 g

[c]Assumes that the average associated gas in the US has the same average composition as the Ohio-associated gas (see Table 1) with an energy content of 40.56 MJ/m³

are typically referred to as fugitive emissions. Table 3 summarizes the typical, average fugitive emissions of associated gas generated during oil production at the oil wellhead [34, 35]. About 0.85% of the CH_4 in the associated gas is emitted as fugitive emissions during the oil drilling and collection which averages 0.163 g/MJ. Since these associated gas processes require energy, the associated CO_2 emissions are 2.01 g/MJ.

Synthetic fuel production and distribution

The synthetic fuel is produced using the Greyrock Flare-to-Fuels™ process. The plant employed for the Ohio well is one of Greyrock's modular conversion plants that can convert from 1.42×10^3 to 5.66×10^4 m³/day of associated gas directly to liquid fuels [36, 37]. For this LCA study, the Greyrock plant used 2.38×10^4 m³/day of associated gas for the plant operation and fuel production. The Greyrock Ohio plant produces directly about 11,007 L/day of fuel, resulting in an average plant thermal efficiency of approximately 58% (when calculating efficiency using feedstock to the plant) or a conversion efficiency of approximately 44% when all gas inputs (including feedstock and gas for parasitic/burner loads) are used in the calculation. This

fuel comprises 8,694 and 2,313 L/day of synthetic diesel and synthetic gasoline, respectively.

Figure 1 illustrates the primary unit operations for the Greyrock process. The associated gas feedstock is input into the system **101**. Other gas-phase feedstocks that can be converted directly to fuels directly by the Greyrock process include bio-gas; gas-phase hydrocarbons (for example, C_2–C_6); natural gas liquids (NGL); individual components extracted from natural gas streams such as ethane, propane, butane, or others, natural gas condensates (C_{5+}); or liquids (such as naphtha, or glycerol from biodiesel plants) that can be easily vaporized into a gas. Any adverse contaminants, such as sulfur compounds, are removed **102** from the gas-phase hydrocarbons before input to the syngas generator and/or after the production of the syngas. The contaminant removal process can vary depending on the composition and quantity of contaminants. For this LCA, sulfur species are absorbed over solid phase media, such as zinc oxide. Syngas can be generated **103** can use a variety of methods, but in this configuration, catalytic steam methane reforming is used to convert the associated gas to syngas.

Following syngas generation, the syngas is directly converted to liquid fuels using Greyrock's GreyCat™ direct fuel production catalyst **104**. The liquid fuel consists primarily of premium synthetic diesel fuel with smaller quantities of synthetic gasoline fuel.

The liquid fuels **105** can be used directly and locally **106** in off-road diesel engines such as diesel generators, tractors, compressors, water pumps, farm equipment, construction equipment, etc., by blending at 20 vol% with petroleum diesel. It can also be transported by truck and/or rail **107** to a nearby central location, where it can be distilled into synthetic diesel and gasoline fractions and blended, respectively, with petroleum diesel and gasoline or used neat in the case of diesel. It is then distributed to local fueling stations **108**.

The GHG emission burdens were allocated among the fuel products according to their energy output shares of the plant. This was accomplished by applying the direct energy

Table 3 Fugitive emissions of associated flare gas at the wellhead during oil production

Oil production processes	CH₄ emissions		CO₂ emissions
	% of Total	g/MJ[a,b]	g/MJ[a,b]
Oil drilling	0.40%	0.077	–
Gas collection and transfer to the co-located synthetic fuel production plant	0.45%	0.086	2.01
Total	0.85%	0.163	2.01

[a]Determined using 21.11 g of hydrocarbons per MJ for 2.38×10^4 m³ of the Ohio-associated gas with an average energy content of 40.56 MJ/m³
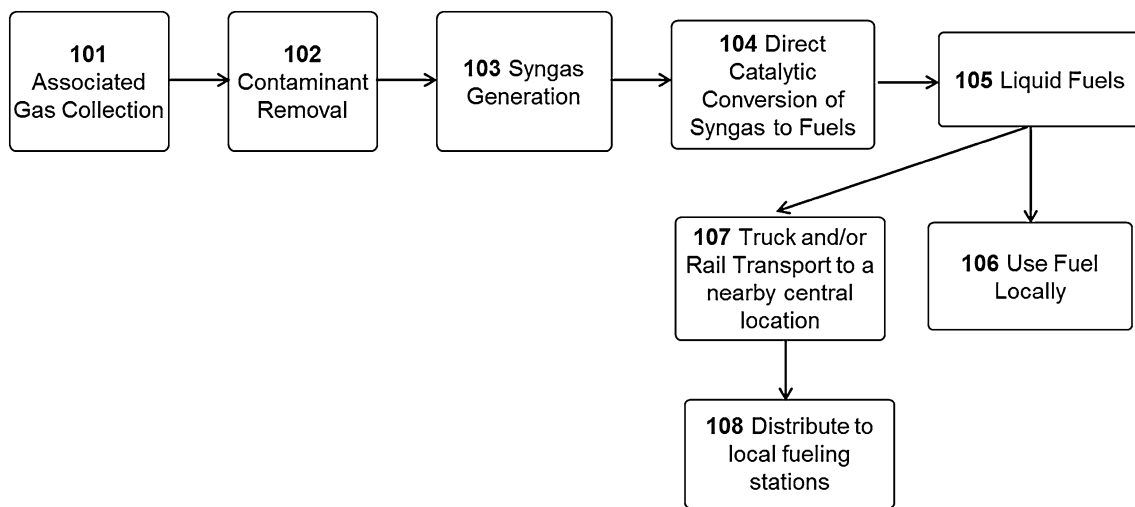
[b][References 34, 35]

Fig. 1 General plant process flow diagram used for conversion of the associated flare gas to synthetic fuels at the Ohio base case wellhead

allocation method. Energy outputs were determined using the corresponding lower heating values (LHV). The production of hydrocarbon fuels requires the consumption of various resources, including makeup water, heat, and power for plant operation. In addition, the process also generates emissions and waste products. The material and energy flows (hereafter referred to as the life cycle inventory or LCI) from the Greyrock Flare-to-Fuels™ process were used for the LCA (Table 4).

Further details on the air emissions from the Greyrock's unit processes are provided in a DOE report [25]. This LCI does not include the energy used for building the plant (the plant infrastructure) which is not significant, since the plant has a lifetime of about 20 years (or more).

The associated gas inputs to the plant are 13.26 and 10.54 m³/day for plant operation and fuel production, respectively. The total associated gas input is 19.23 with 10.70 g/MJ used for plant operation and 8.53 g/MJ for fuel production resulting in an energy efficiency of plant thermal efficiency of approximately 58% (when calculating efficiency using feedstock to the plant) or a conversion efficiency of approximately 44% when all gas inputs (including feedstock and gas for parasitic/burner loads) are used in the calculation. Plants may also produce excess power from waste steam, improving efficiency.

Water is needed (3531 L/day) for conversion of the associated gas to syngas (H_2 and CO) in the syngas generator. The direct catalytic conversion of the syngas to fuels produces water which is recycled directly to the syngas generator.

Some associated gas (537 GJ/day) is used for the high efficiency, low emission gas burners [38] and the production of plant power. The plant air emissions are summarized in Table 4.

The distribution of the Greyrock synthetic fuel was established to meet the objectives of the United Nations Sustainable Consumption and Production objectives [39] which

Table 4 Performance specifications for the Greyrock-associated flare gas to synthetic fuels production plant at the Ohio oil wellhead

Associated gas inputs	MJ/day	g/day[a]	G/MJ
Plant operation	5.37×10^5	1.13×10^7	11.79
Fuel production	4.27×10^5	9.01×10^7	9.37
Total	9.64×10^5	2.04×10^7	21.16
	L/day	g/day	g/MJ
Plant inputs			
Water	3531	3.53×10^6	3.66
Synthetic fuel production			
Synthetic diesel	8694	6.65×10^6	6.89
Synthetic gasoline	2313	1.58×10^6	1.64
Total synthetic fuel output	11,007	8.23×10^6	8.53
Synthetic fuel distribution			
20 vol% diesel blends	43,471	3.56×10^7	36.9
10 vol% gasoline blends	23,126	1.50×10^7	15.5
Plant air emissions	–	g/day	g/MJ
Methane (CH_4)	–	4.53×10^2	9.16×10^{-4}
Carbon dioxide (CO_2)	–	2.57×10^7	5.20×10^2
Carbon monoxide (CO)	–	3.33×10^2	6.20×10^{-4}
Particulate matter (PM)	–	4.16×10^2	7.75×10^{-4}
Nitrogen oxides (NOx)	–	5.55×10^2	1.03×10^{-3}
Non-methane hydrocarbons (NMHC)	–	2.17×10^3	4.38×10^{-3}

[a]Value determined using 21.16 g/MJ of hydrocarbons for the Ohio gas

encourage local production local consumption (LPLC) approaches for energy and fuels. The LPLC methodology uses less energy than the current process of shipping or pipping petroleum oil long distances to huge refineries and then distributing the fuel products long distances to fueling stations. It is estimated that the energy required for petroleum oil transport and fuel distribution is reduced conservatively by about 75% compared to that of petroleum refineries.

The local distribution of the synthetic fuel is dependent upon the location of the synthetic fuel production site and the types of diesel equipment and vehicles in which it will be utilized. The following distribution scenarios were employed in the LCA model.

Synthetic fuel properties

All of the synthetic fuels, produced at the wellhead site, can be used directly (without distillation) in off-road diesel equipment and vehicles if it is blended at about 20 vol% with petroleum diesel. This is essentially done by splash blending the synthetic fuel in the fuel tank or using a proportional fuel distribution system that blends the synthetic and petroleum diesel in the correct proportions as it is being pumped into the fuel tank. This blend is typically used within 30–40 km miles of the production site. However, it was decided that this study would focus on the separation of the liquid fuel into synthetic diesel and gasoline fractions for use in "on-the-road" vehicles.

To meet fuel volatility specifications for on-the-road vehicles (i.e., flash point for diesel and Reid Vapor Pressure for gasoline), the fuel is separated (distilled) into diesel and gasoline fractions. The distribution between the diesel and gasoline distillates is typically 79 and 21 vol%, respectively. The distribution of the fuels from the bulk terminal to local refueling stations was assumed to be 100% by truck [36, 37] and within about 320 km of the bulk terminal.

Table 5 summarizes the properties for the Greyrock pure synthetic diesel and synthetic gasoline fuels, the 20 vol% Greyrock synthetic diesel blend with petroleum #2 diesel fuel, and the 10 vol% Greyrock synthetic gasoline blend with 91 Octane petroleum gasoline fuel. The Greyrock synthetic diesel fuel meets or exceeds diesel fuel specifications established by ASTM D975, and it has similar chemical and physical properties to diesel fuels typically produced from Fischer–Tropsch (F–T) processes in multi-billion dollar plants operated by Shell and Sasol [40–42], except that the Greyrock synthetic diesel fuel has much better lubricity (371 vs. 650 μm) and higher storage stability (0.1 vs. 0.4) than the Shell and Sasol synthetic diesel fuels. As a result, there is less engine wear when a diesel fuel has a high degree of lubricity, resulting in increased diesel engine life. Since the basic chemical composition of the Greyrock synthetic diesel fuel is very similar to that of the Shell and Sasol synthetic diesel fuels, they perform the same in terms of engine power output, fuel economy, and emission reduction [43].

Table 5 Comparisons of properties of Greyrock synthetic fuels with EPA petroleum fuels and blends of the Greyrock synthetic fuels with the EPA petroleum fuels

Diesel fuel properties (ASTM test reference)	Greyrock synthetic Diesel	Petroleum #2 diesel	Greyrock synthetic blend (20 vol%)	Shell and sasol synthetic diesel
Cetane Index (D976)	75	45	51	75
Lubricity (μm) (HFRR) (D6079)	371	520[a]	404	650
Sulfur (ppm)	< 0.1	15	12	< 1.0
Aromatics (%)	< 0.1	20	16	< 1.0
Flash point (FP) (°F) (D93)	100	126	120	120
Energy content (LHV) (MJ/L)	28.73	29.82	29.60	28.73
Density (g/mL)	0.765	0.840	0.820	0.765
Oxidative stability (D2274)	0.1	1.5	1.2	0.4

Gasoline fuel properties	Greyrock synthetic gasoline	Petroleum gasoline	Petroleum gasoline with 10% Greyrock gasoline	Petroleum gasoline with 10% ethanol
Octane rating	63	91	89	91
Energy content (LHV) (MJ/L)	27.04	26.48	26.54	25.82
Reed vapor pressure (RVP) (psi)	9.0	9.0	9.0	9.0
Density (g/mL)	0.680	0.645	0.656	0.660

[a]Fuel lubricity measured before the addition of lubricity agents

Since the Greyrock synthetic diesel has a much longer storage lifetime than traditional petroleum diesel fuel, it can be stored for several years without degradation. This extended storage stability is in part, because the Greyrock diesel does not contain interior olefins (2, 3 and 3, 4 olefins) and other fuel constituents that can easily oxidize during storage in fuel tanks and fuel lines [25, 44]. It has been confirmed that this fuel is very stable and that no chemical or physical changes occur even when it is stored at room temperature for more than 5 years in ambient light. It is well known that when petroleum diesel degrades during storage, peroxides and deposits are formed which shortens the lifetime of diesel engines [45].

The Greyrock synthetic diesel has a lower density (0.76 g/ml compared to 0.84 g/ml for petroleum diesel) and viscosity than current fuels resulting in improved high-pressure fuel injector fuel spray formation, enhanced combustion efficiency, and improved engine performance. Other potential benefits include improved cold starts and fuel economy, reduced warm-up time, fewer misfires and lower exhaust emissions of nitrogen oxides, hydrocarbons, carbon monoxide, and particulate matter [46–52].

A 20 vol% blend of the Greyrock synthetic diesel with EPA #2 petroleum diesel increases the cetane of the EPA #2 diesel from 45.0 to 51.0. A cetane of about 51–53 is the optimum cetane value for most diesel engines and increases above this level has a diminishing effect on the improvement of engine operation and reduction in emissions [53, 54]. The 20 vol% synthetic diesel blend lowers the concentration of sulfur and aromatics compared to EPA #2 diesel fuel (Table 5) which results in reduced emissions.

Table 5 also summarizes some of the properties of the synthetic gasoline. The synthetic gasoline has an octane rating of 63 which limits the volume that can be blended with petroleum gasoline. A 10% blend of the synthetic gasoline with 91 octane gasoline results in an octane rating of 89 which is a suitable octane level for more than 95% of gasoline engines. The 10% Greyrock blend has an energy content of 26.54 MJ/L compared to 25.82 MJ/L for petroleum

gasoline blended with 10% ethanol. Therefore, although the 10 vol% Greyrock blends should improve fuel economy by 2.7%, engine dynamometer tests have not been carried out to validate this potential improvement in fuel economy. Although the 10 vol% Greyrock synthetic gasoline blend should result in a small reduction in criteria emissions due to lower sulfur and aromatic content, these reductions were not included in the WTW-LCA modeling.

WTW-LCA emission modeling

Argonne National Laboratory's GREET LCA Model [33] was used to quantify and account for the GHG emissions. Greyrock's Flare-to-Fuels LCA model was used to quantify and account for criteria pollutant emissions over the entire WTW supply chain. Figure 2 shows the life cycle system boundary for this study. The WTW life cycle system includes: (1) wellhead associated gas collection; (2) wellhead direct synthetic fuel production; (3) synthetic fuel distribution in local markets; and (4) synthetic fuel use (combustion) in vehicles. The LCA results for stages 1–4 were compared with (5) wellhead associated gas flaring to determine the reduction in GHGs and criteria air pollutants. Unless mentioned in the subsequent description of the life cycle stages below, we made use of the GREET inventory associated with the upstream (such as CH_4 leakage during natural gas recovery) and downstream processes (such as vehicle operation). Only the activity inventory for the synthetic fuel production step is provided by Greyrock and not from GREET. Furthermore, the GHG emission factors are all based on the default values in GREET.

GHG emissions in this study were expressed as carbon dioxide equivalents (CO_{2e}) in g/MJ of associated gas using CH_4 that has 84 and 34 times more heat-trapping ability than CO_2 over 20- and 100-year periods, respectively. The WTW GHG emissions in g/MJ were determined from Eq. 1 for the 20-year period and Eq. 2 for the 100-year period:
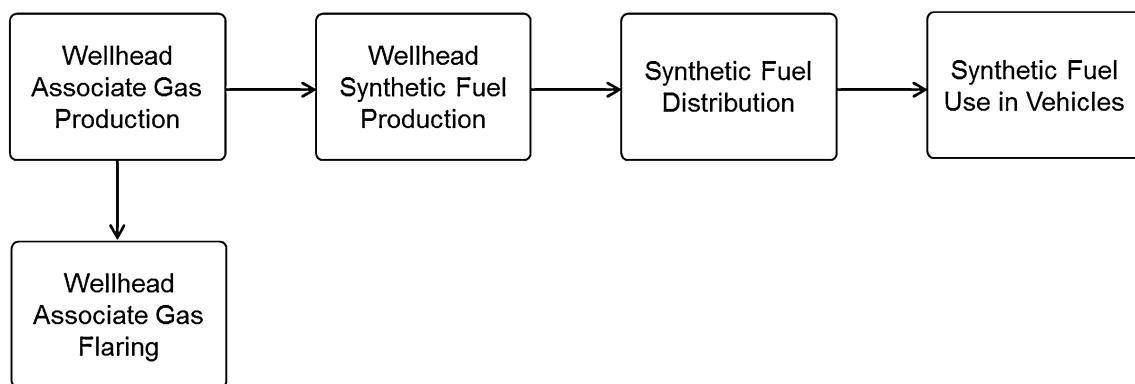
$$CO_{2e} = 84 \left[CH_4 \right] + CO_2, \tag{1}$$

Fig. 2 Life cycle assessment used for the well-to-wheel pathway

$$CO_{2e} = 34 \left[CH_4 \right] + CO_2. \tag{2}$$

The average composition of associated gas from the Ohio base case well (Table 1) was used for this LCA. The associated gas produced from this oil well has an energy content of 40.56 MJ/m³. The plant used 2.38×10^4 m³/day of associated gas available from this oil well.

Results

The results of the WTW-LCA from flared associated gas for the three scenarios (a typical well in Ohio, and existing flares in the US, and globally); the volume of synthetic fuels that could be produced for these three scenarios; the reduction in emissions by converting this associated gas directly to synthetic fuels at the wellhead; and the reduction in vehicle emissions from using the synthetic fuels in diesel vehicles are described. The importance of these findings for the mitigation of global GHGs and reduced environmental impact from criteria pollutants in ambient air are discussed.

Associated gas flare emissions

The fugitive emissions CH_4 and CO_2 for associated gas at the base case Ohio wellhead are summarized in Table 3. The fugitive CH_4 emissions included 0.163 g/MJ from oil drilling and gas collection. The CO_2 emissions are 2.01 g/MJ.

EPA recommended in 2013 that a flare efficiency of 98% be accepted as an emission factor [55]. This flare efficiency was primarily established for relatively new flares that incorporated new technologies including air-to-fuel ratio control systems. However, the efficiency of associated gas flares varies from 70 to 99%, depending upon the type and age of the flare, the composition and flow rate of the associated gas; the air-to-fuel ratio of the flare combustion; and atmospheric conditions [56–59].

Since the EPA recommendations, several comprehensive studies have been carried out to measure the efficiency of flaring associated gas from actual wells, and some of these results are summarized in Table 6 [56, 57]. The average flare efficiency for these studies is 95%. Other investigators have also adopted this 95% efficiency value [58, 59]. Therefore, an average flare efficiency of 95% was used for this study.

Since the volume of the Ohio-associated gas is 2.38×10^4 m³/day and 87.9% of the gas is methane, then the volume of methane is 2.09×10^4 m³/day. Therefore, the emission of methane is calculated from Eq. 3, using a flare efficiency of 95% and an associated gas energy content of 9.64×10^5 MJ/day:

$$\left[\left(2.09 \times 10^7 \text{ L/day} \right) / \left(22.4 \text{ L/mole} \right) \right] \left(16 \text{ g/mole} \right) \left(5\% \right) / \left(9.64 \times 10^5 \text{ MJ/day} \right)$$

$$= 0.773 \text{ g/MJ}. \tag{3}$$

Table 6 Results of efficiency studies for associated gas flares in the US

Well location	Reference	Flare combustion efficiency (%)
Tennessee	Willis [22]	95.5
Georgia	Willis [22]	94.5
North Dakota	Gvakharia [23]	95.1
Average	–	95.0

Table 7 Effect of flare operating conditions on emissions of associated gas at the base case Ohio oil wellhead under various Lambda ratios and hydrocarbon conversion efficiencies (EFF)

Emission constituents	Flare conditions		
	Lambda: 1.00 EFF: 99.5%	Lambda: 1.10 EFF: 95%	Lambda: 0.90 EFF: 95%
	Emissions (g/MJ)		
CO_2	55.2	52.3	52.3
CO	0.117	0.74	3.62
NOx	0.140	38.7	6.67

The total methane emissions include 0.773 g/MJ from flaring and 0.163 g/MJ (see Table 3) from fugitive emissions at the oil well for a total of 0.936 g/MJ.

The emissions of CO_2 are calculated from the combustion of CH_4, C_2H_6, C_3H_8, C_4H_{10}, and C_5H_{12} in the Ohio-associated gas using the 95% flare efficiency value. Therefore, the CO_2 emissions are 46,440 g from CH_4; 6,184 g from C_2H_6; 3,327 g from C_3H_8, 2,785 g from $C_4H_{10;}$ and 1,044 g from C_5H_{12}. Since the Ohio gas contains 0.5% CO_2 or 278.1 g, this quantity is added to the CO_2 produced from the combustion of the hydrocarbons for a total of 60,058 g or 21.1 g/MJ.

Associated gas flares also produce particulate matter (PM) (e.g., black carbon), NOx, non-methane hydrocarbons (NMHC), SO$_x$, and air toxics. Ismail and Umukoro [60] have developed kinetic equations for predicting the emissions of CO_2, CO, NO, NO_2, and SO_2 from gas flaring. They demonstrated that the concentration of these emissions depends primarily on the ratio of air/fuel (A/F) hydrocarbons in the flare, flare gas composition, and flare combustion efficiency. Table 7 summarizes the effect of three different operating conditions on flare emissions of the associated gas at the base case Ohio oil wellhead using these models. It was found that NOx emissions are higher under lean conditions (Lambda = 1.10) than under rich conditions (Lambda = 0.90), whereas CO emissions are reduced under lean conditions.

Weyant et al. [6] measured black carbon (BC) emissions from 26 individual flares in the North Dakota Bakken formation and established that flare-generated particulate matter

(PM) is predominantly black carbon (BC). They estimated the BC emission factors from light absorption measurements and calculated an emission factor of about 3.1 g BC per kg of associated gas hydrocarbons. Since the Ohio-associated gas contains 21,824 g of hydrocarbons per 28.3 m^3, the emission factor is 771.2 g/m^3 or 21.16 g/MJ.

McEwen et al. [61] determined BC emission factors for associated gas flares and determined an emission factor of 2.47 g/m^3 or 0.059 g/MJ. The Canadian Association of Petroleum Producers (CAPP) [62] recommended a particulate matter (PM2.5) emission factor of 2.56 g/m^3 or 0.063 g/MJ, as based on a US Environmental Protection Agency (EPA) factor for landfill gas flares attributed to filterable PM measurements [63]. These three measurements are in good agreement, and therefore, the average value of 0.061 g/MJ was used in the LCA model. On the average, the PM from flares is comprised of about 90% elemental carbon (black carbon) and 10% solvent extractable materials.

Stohl et al. [17] estimated that this amount of black carbon (BC) from flaring in the Northern Hemisphere contributes 42% to the annual mean BC surface concentrations in the Arctic. The deposit of this BC on ice and snow intensifies the absorption of solar heat which increases melting. This results in enhancing global warming in the arctic which introduces secondary effects such as the release of methane from methane hydrates [13].

The emissions of sulfur dioxide (SO_2) were determined assuming that all hydrogen sulfides (H_2S) were oxidized to SO_2 in the flare according to Eq. 4. Since the Ohio flare gas contained 0.007 vol% of H_2S, then the SO_2 emissions are 0.49 g/MJ:

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O. \tag{4}$$
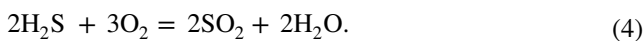
The emission of nitrogen oxide (NOx) from associated gas flares is primarily a function of the gas composition; the air-to-fuel ratio (A/F); the combustion temperatures and pressures; and residence time in the combustion zone. NOx is comprised of nitrous oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O) species. Although N_2O is 310 times more efficient in terms of global warming than CO_2 [19, 20], this gas was not included as a GHG in this LCA study, since its average concentration in flare gas emissions has not been adequately quantified. Table 8 summarizes these GHG and criteria emissions for associated flare gas at the base case Ohio wellhead in g/day and g/MJ.

Synthetic fuel diesel emissions

Table 9 provides the average reduction (%) of vehicle emissions when synthetic diesel fuel is blended with petroleum diesel at 20 vol%, used as is (100%), and tested in four categories (II–V) of diesel vehicles [46–53, 64–71]. The emission reductions with the synthetic fuels are

Table 8 LCA modeling results for GHG and criteria emissions for associated flare gas at the base case Ohio oil wellhead

Constituents	Emissions	
	g/day	g/MJ[a]
CO	3.49×10^6	3.62
Particulate matter (PM)	5.87×10^4	0.061
Sulfur dioxide (SOx)	4.76×10^5	0.49
Nitrogen oxides (NOx)	6.44×10^6	6.67
Hydrocarbons	9.28×10^5	0.96
CH_4	9.08×10^7	0.94[b]
CO_2	5.33×10^7	55.2
$CO_{2eq.}$ (100 year model)[c]	8.32×10^7	87.2
$CO_{2eq.}$ (20 year model)[d]	1.28×10^8	134.2

[a]The total associated gas input is 2.38×10^4 m^3/day that has 19.23 g/MJ of hydrocarbons in the associated gas with an energy content of 40.56 MJ/m^3. The emissions are determined using an average flare efficiency of 95% for combustion of the flared associated gas. The associated gas energy input is 963,900 MJ/day

[b]The total CH_4 emissions include 0.773 g/MJ from flaring and 0.163 g/MJ from fugitive emissions at the oil well (Table 3)

[c]The 100-year $CO_{2eq.}$ calculation uses an atmospheric heat-trapping capability for CH_4 that is 34 times greater than that of CO_2

[d]The 20-year $CO_{2eq.}$ calculation uses an atmospheric heat-trapping capability for CH_4 that is 84 times greater than that of CO_2

compared to a baseline of using petroleum #2 diesel fuel. The choice of these categories is based upon the type of engine control system designed to meet Euro 2 [Category II], Euro 3 [Category III], Euro 4 [Category IV], and Euro 5 [Category V] emissions standards [72, 73].

Although most of the emission tests summarized in Table 9 were carried out with synthetic diesel fuels produced from very large plants operated by Sasol, Shell and others, the chemical compositions of these synthetic diesel fuels are very similar to Greyrock's fuel (Table 5), and therefore, these average emission reductions were used in the WTW-LCA model.

As presented in Table 9, although the diesel vehicles in categories II–V had different engines and control systems, the 100% synthetic diesel blend provided relatively similar average emissions reduction levels for PM, NOx, CO, HC, CH_4, and CO_2. The cetane levels of the 10, 20, 50, and 80% blends were 48, 51, 60 and 69, respectively. There is a significant reduction in diesel emissions up to the 20 vol% blend level with less significant improvement for the pure synthetic fuel.

Figure 3 illustrates the average reduction in emissions for the Category V (2011–2015) diesels when synthetic diesel (cetane: 75) is blended with petroleum #2 diesel (cetane 45) at different blend levels. These 2011–2015 diesel vehicles are equipped with emission control technologies that comply

Table 9 Average emission reduction (%) for four categories of diesel vehicles when synthetic diesel is blended at 20 vol% with EPA #2 petroleum diesel fuels and compared to the emissions from 100% EPA #2 petroleum diesel fuels

Categories of diesel vehicles (model years) [emission control systems][a]	Average emissions reduction (%)					
	PM	NOx	CO	HC	CH$_4$	CO$_2$
20% synthetic fuel blend with EPA #2 petroleum diesel compared to 100% EPA #2 petroleum diesel						
Category II (1996–2000) [Euro 2]	20	5	27	27	–	2.0
Category III (2000–2005) [Euro 3]	15	7	31	24	–	1.6
Category IV (2005–2011) [Euro 4]	18	6	18	34	–	1.4
Category V (2011–2015) [Euro 5]	18	4	18	26	11	0.9
Average	18	5.5	24	28	11	1.5
100% Synthetic Fuel compared to 100% EPA #2 Petroleum Diesel						
Category II (1996–2000) [Euro 2]	31	11	30	44	–	5
Category III (2000–2005) [Euro 3]	21	10	36	40	–	2
Category IV (2005–11) [Euro 4]	31	7	38	56	–	7
Category V (2011–2015) [Euro 5]	32	14	35	55	21	5
Average	29	10.5	35	49	21	4.8

[a]Data derived from references [46–53, 64–71] and Greyrock's emissions studies

with Euro 5 emission standards for CO, particulate matter (PM), NOx, and non-methane hydrocarbons (NMHCs). These emission standards are summarized in Table 10 (column 1) for petroleum #2 diesel fuel in g/km.

In North America, most states have adopted ASTM D975 as their diesel fuel cetane number (CN) standard with typical values in the 42–45 range. In general, diesel engines operate best with a CN of 50–52. Fuels with lower CN have longer ignition delays, providing more time for the fuel combustion process to be completed. Hence, higher speed diesel engines operate more effectively with higher CN fuels [54].

As a result, the emissions data for the 20 vol% blend were used in this model, since its cetane of 51 is nearly ideal and the emissions reduction for PM, NO$_x$, CO, HC, and CH$_4$, are

62, 52, 69, 57, and 52%, respectively, compared to emissions from the 100% synthetic fuel.

Table 11 summarizes the average fuel economy in miles per gallon (mpg) for several types of 2016–2017 passenger vehicles with 1.6–2.0-L engines using a driving cycle that is representative of 55% city and 45% highway driving [73–75]. Although gasoline/electric and diesel/electric hybrids have much better fuel economy than their non-hybridized counterparts, the hybrid vehicles were not employed in this modeling study, since their share in the vehicle fleet is still relatively small.

The GREET 2013 uses an average on-road fuel economy of 11.9 km/L for spark ignition (SI) gasoline vehicles and a similar on-road fuel economy of 11.9 km/L for compression–ignition direct-injection (CIDI) diesel vehicles. Current

Fig. 3 Average reduction in emissions from 2011 to 2015 diesels (Euro 5 emissions control) when synthetic diesel is blended with petroleum #2 diesel at various blend levels
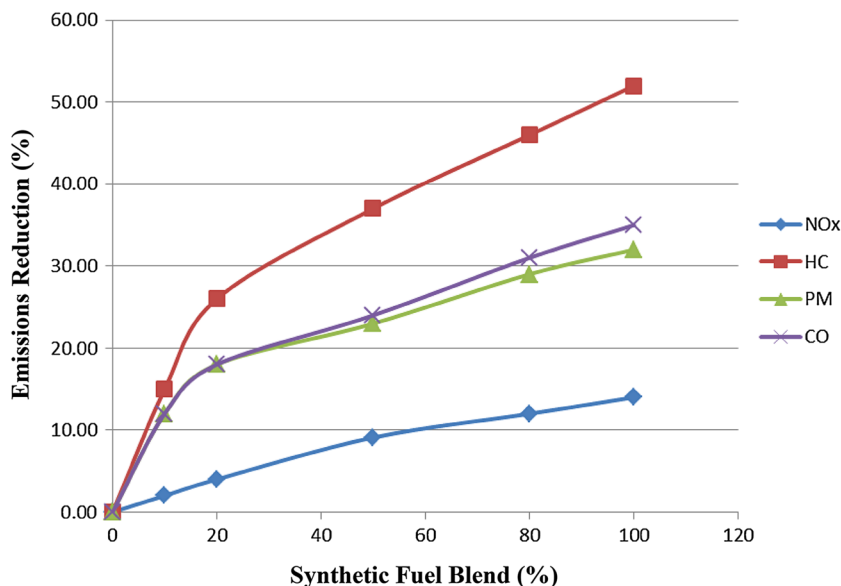
Table 10 Average GHG and criteria emissions for 2011–2015 light-duty diesel passenger vehicles (1.6–2.0 L engines) with Euro 5 emission control (or equivalent) using a 20% blend of synthetic diesel with EPA #2 diesel fuel

Constituent	Emissions (g/km)[a]	Emissions (g/day)[b]		
	Petroleum #2 diesel fuel	Petroleum diesel fuel[c]	20% blend of synthetic diesel with #2 diesel[d]	Reduction
Criteria pollutants				
CO	5.0×10^{-1}	3.61×10^{5}	2.96×10^{5}	6.94×10^{4}
PM	5.0×10^{-3}	3.61×10^{3}	2.96×10^{3}	6.49×10^{2}
NOx	1.8×10^{-1}	1.30×10^{5}	1.25×10^{5}	5.20×10^{3}
HC	5.0×10^{-2}	3.61×10^{4}	2.67×10^{4}	9.38×10^{3}
Greenhouse gases (GHGs)				
CH_4	1.24×10^{-2}	8.95×10^{3}	7.96×10^{3}	9.48×10^{2}
CO_2	1.71×10^{2}	1.23×10^{8}	1.22×10^{8}	1.11×10^{6}

[a]Based upon Euro 5 emission standards [Reference 72]

[b]Determined for light-duty diesel vehicles with 1.6–2.0 L engines having an average fuel economy of 16.6 km/L (see Table 11), consuming 43,471 L of the 20% Greyrock synthetic diesel blend (1 day of synthetic diesel fuel production at the Ohio well) and with those vehicles traveling a total of 721,619 km in 1 day

Table 11 Average fuel economy for 2015–2017 model-year passenger vehicles with 1.6–2.0 L engines

| Vehicle types	Average fuel economy in km/L (mpg)[a]
Gasoline (spark-ignition engines)	11.9 (28)
Diesel (compression ignition engines)	16.6 (39)
Gasoline hybrid electric vehicles (gasoline HEVs)	19.5 (46)
Diesel hybrid electric vehicles (diesel HEVs)	26.9 (63)
Battery electric vehicles (BEVs)	37.0 (87)

[a]Combined rating for 55% city driving and 45% highway driving [References 73–77]

model light-duty gasoline vehicles (2015–2017) have an average fuel economy of 11.9 km/L which is similar to that used in the Argonne GREET model. However, current light-duty diesel vehicles have about 39% better fuel economy [16.6 km/L than comparable gasoline vehicles (Table 11)].

Since there are 121.7 and 135.8 MJ (lower heating value) in a gallon of gasoline and diesel fuels, respectively, these current fuel economies correspond to a total fuel energy use of 1.85 and 1.52 MJ/km for gasoline and diesel engines, respectively. Therefore, current diesel vehicles consume 21.5% less energy than comparable gasoline vehicles. Life cycle impacts related to the vehicle production, servicing, and end-of-life were not included in this LCA.

Light-duty diesel CO_2 emissions were determined from Eq. 5 for the Greyrock fuel which has a density of 765.1 g/L and an average fuel molecular weight of 170 g/mol. Therefore, the CO_2 emissions average 143.4 g/km. CH_4 emissions of 1.24×10^{-2} g/km for light-duty diesels are used as

reported by Lipman and Delucchi [18] and are provided in Table 10:

$$2C_{12}H_{26} + 37O_2 = 24CO_2 + 26H_2O. \qquad (5)$$
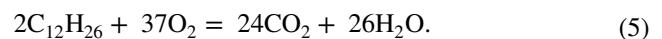
The plant directly produces 11,007 L/day of fuel which is distilled into 8694 and 2313 L of diesel and gasoline blendstocks, respectively. The 8694 L of synthetic diesel is blended with 34,777 L of petroleum diesel to produce 43,470 L of a 20 vol% synthetic diesel blend each day or 15,866,720 L/year. Since the average 2015–2016 light-duty (1.6–2.0 L) diesel car has an average fuel economy of 16.6 km/L, then this Ohio well can produce enough fuel for 263,387,550 km of light-duty diesel vehicle travel. Since the average American drives an average of 21,683 km/year [35], this is enough fuel for about 12,096 diesel cars each year. If all the associated flare gases in the US are converted to diesel fuel and blended at 20 vol% with petroleum diesel that would be enough fuel for about 30,293,000 diesel vehicles each year.

WTW-LCA GHG emissions

Table 12 summarizes the GHG emissions from the WTW-LCA model when associated gas is not flared but instead converted directly to synthetic fuels at the oil wellhead. The % GHG reduction in g CO_{2e}/MJ was calculated by totaling the GHG emissions for: (1) associated gas production; (2) synthetic fuel production; (3) fuel distribution; (4) vehicle fuel use; and (5) adding the flaring credit.

The GHG emissions for the collection of the associated gas were determined from fugitive losses of CH_4 and CO_2 during removal and transfer of the gas from the wellhead to the co-located synthetic fuel production plant which correspond to 16.6 and 8.0 g CO_{2e}/MJ using the 20- and 100-year

LCA lifetime models, respectively. Since a similar loss of CH_4 and CO_2 occurs during removal and transfer of the gas from the wellhead during oil production, the GHG emissions for the petroleum gasoline and petroleum diesel are comparable.

The GHG emissions for the flare are 134.2 and 87.2 g CO_{2e}/MJ using the 20- and 100-year WTW-LCA model, respectively, as based upon a flare combustion efficiency of 95.0%. Since flare gas would otherwise be flared and emitted to the atmosphere, 134.2 and 87.2 g/MJ of avoided GHG flare emissions are included as credits in the LCA.

The GHG emissions for the direct production of fuel from associated gas using the Greyrock Flare-to-Fuels™ process are 51.6 g CO_{2e}/MJ compared to 11.6 and 11.4 g CO_{2e}/MJ for the production of petroleum gasoline and diesel using the 20- and 100-year WTW-LCA model, respectively.

The transport of the finished fuel product to the customer is much less for the flare gas-derived synthetic diesel fuel than the petroleum gasoline and diesel (0.30 vs. 1.20 g CO_{2e}/MJ), since the fuel distillation, blending, and distribution of the synthetic fuel are much closer than trucking, railing, and piping oil to large refineries and distributing the fuel over a wide region.

The GHG emissions of 51.6 g CO_{2e}/MJ for the synthetic diesel fuel are less than that for petroleum diesel fuel (52.8 g CO_{2e}/MJ), since the synthetic diesel fuel provides improved fuel economy and reduced emissions of CO_2 and CH_4 compared to petroleum diesel. The reduction in GHG emissions of 52.8 and 52.6 g CO_{2e}/MJ for petroleum diesel, using the 20- and 100-year lifetime models, respectively, is nearly the same, since the emissions of CH_4 from diesel vehicles are small compared to CO_2 emissions.

Since 2016–2017 light-duty (1.6–2.0 L) diesel vehicles have an average fuel economy of 39 mpg compared to 28 mpg for comparable spark-ignition gasoline vehicles (Table 11), petroleum diesel vehicles yield a reduction in GHG emissions by 20.5% compared to gasoline vehicles and synthetic diesel vehicles reduce GHG emissions by 21.7% compared to gasoline vehicles.

WTW-LCA criteria emissions

Table 13 summarizes the potential reduction in criteria emissions compared to GHG emissions in the US and globally when associated flare gas is converted directly to synthetic fuels at the oil wellhead. These criteria air pollutant emissions could be reduced in the US up to 3.44, 0.060, 6.31, and 0.91 million tons/year for CO, PM, NOx, and HCs, respectively, and reduced globally by up to 45.9, 0.80, 84.1, and 12.2 million tons/year for CO, PM, NOx, and HCs, respectively.

The direct conversion of associated gas to synthetic fuels at oil wellheads in the US could reduce the emissions of CO_2 and CH_4 by 26.8 and 0.45 million tons, respectively, resulting in the reduction of GHGs by about 113.3 and 92.2% (20 year global warming potential) and 73.8 and 50.7% (100 year global warming potential) when compared to petroleum-derived gasoline fuels, respectively. Globally, the emissions of CO_2 and CH_4 could be reduced by up to 356 and 5.96 million metric tons, respectively (Table 13).

Discussion

The LCA model employed in this study used average US-associated gas flare efficiencies of 95%. However, flare efficiencies may be as low as 65–75%, especially in some

Table 12 Reduction in WTW-LCA GHG emissions when associated flare gas is directly converted to synthetic fuels at the oil wellhead

Scenario	Flaring credit	Associated gas production	Produce synthetic fuel	Distribute fuel	Vehicle fuel use	WTW	% GHG reduction
GHG emissions (g CO_{2e}/MJ) for 20-year lifetime							
Petroleum gasoline	–	16.6	11.6	1.20	73.3	102.7	–
Petroleum diesel	–	16.6	11.4	1.20	52.8	82.0	+ 20.2[a]
Flare gas to synthetic diesel	− 134.2	16.6	52.0	0.30	51.6	− 13.7	+ 113.3[a]
Flare gas to synthetic gasoline	− 134.2	16.6	52.0	0.30	73.3	8.0	+ 92.2[a]
GHG emissions (g CO_{2e}/MJ) for 100-year lifetime							
Petroleum gasoline	–	8.0	11.6	1.20	73.3	94.1	–
Petroleum diesel	–	8.0	11.4	1.20	52.6	73.2	+ 22.2[b]
Flare gas to synthetic diesel	− 87.2	8.0	52.0	0.30	51.6	24.7	+ 73.8[b]
Flare gas to synthetic gasoline	− 87.2	8.0	52.0	0.30	73.3	46.4	+ 50.7[b]

[a]GHG reduction compared to petroleum gasoline for 20-year lifetime

[b]GHG reduction compared to petroleum gasoline for 100-year lifetime

regions of the Middle East; Africa and South America [78–82].

NOAA and the World Bank Global Gas Flaring Reduction Partnership used an NOAA satellite equipped with advanced sensors to estimate the level of global flaring during 2015. It was determined that 147 bcm of associated gas were flared in 2015, compared to 145 bcm in 2014 and 141 bcm in 2013 [82]. Russia is the world's largest gas flaring country, flaring about 21 bcm annually, followed by Iraq (16 bcm), Iran (12 bcm), the US (11.8 bcm), Venezuela (9 bcm), Nigeria (8 bcm), and China (2 bcm) during 2015 [83]. These flare volumes are in good agreement with the 2016 US and global flare volumes of 11.2 and 150 bcm, respectively, that are used in our LCA model.

The US and Russia have the highest number of individual flare sites at oil production wells at 2159 and 948 flares, respectively. Since the US and Russia flared 11.2 and 21.2×10^9 m³/year in 2016, the volume of gas flared per site by the US and Russia was 5.19 and 22.4×10^6 m³/year, respectively. Therefore, Russia's flares are on the average 4.31 times larger than those in the US. In contrast, the associated gas flow of the Ohio well averages 8.69×10^6 m³/year.

We focused on the use of the 20-year lifetime model, since recently, it has been predicted that adverse GHG emission intensity attributed to CH_4 will likely occur on a much shorter timescale of 15–25 years [13, 14] than originally estimated by the IPCC.

Particulate emissions from associated gas flares could be reduced by up to 374,000 metric tons/year globally by producing fuels directly at the oil wellhead (Table 13). Since about 90 weight percent of these particulate emissions are black carbon (BC), then the emissions of BC are 340,000 metric tons/year for the flaring of 150 bcm of

associated gas. Since the primary sources of associated flare gas emissions (North of 40 Latitude) are the US, Canada, Norway, Poland, and Russia with total flare emissions of 28.6 bcm, then the total emissions of BC in the Northern Hemisphere are given by Eq. 6:

$$(28.6 \text{ bcm}/150 \text{ bcm}) (340,000 \text{ metric tons/year})$$
$$= 64,800 \text{ metric tons/year.} \tag{6}$$

This value of 64,827 metric tons/year of BC emissions during 2016 is in good agreement with that of Stohl et al. [17] who determined that associated gas flares produced about 75,300 metric tons/year of BC emissions in the Northern Hemisphere during 2013. Stohl concluded that this flaring could contribute approximately 50% of the annual mean BC surface concentrations in the Arctic region during that period.

BC potentially has a strong influence on radiative forcing in the Arctic, both via direct and indirect effects in the atmosphere and via albedo changes after deposition on snow or ice [84], and this is possibly one of the reasons that the average temperatures in the Arctic during the winter of 2015–2016 were up to 40 °F higher than normal [13].

CO, NOx, and HC emissions can be reduced by up to 1.74; 3.16 and 0.46 million metric tons/year in the US by producing fuels directly at the oil wellhead (Table 13). NOx and HCs react readily with hydroxy radicals in the atmosphere to produce nitric acid, sulfuric acid, ozone, and photochemical smog [85]. Since the primary chemical process for the destruction of CH_4 in the atmosphere is with hydroxy radicals [86], albeit at a much slower rate than with hydrocarbons, the concentration of atmospheric hydroxy radicals will be reduced by these reactions with NOx, SOx, and HCs resulting in an increased lifetime of CH_4 in the atmosphere.

Table 13 Potential reduction in criteria pollutant and GHG emissions in the US and globally by converting associated flare gas directly to synthetic fuels at the oil wellhead and consuming the fuels in vehicles

Emission constituents	Reduction from elimination of flaring (metric tons/year)	Reduction from synthetic fuel use in vehicles (metric tons/year)	Total reduction (metric tons/year)
United States			
CO	1.71E+06	3.13E+04	1.74E+06
PM	2.90E+04	3.13E+02	2.93E+04
NOx	3.16E+06	2.50E+03	3.16E+06
HC	4.54E+05	4.52E+03	4.59E+05
CH_4	4.45E+05	4.74E+02	4.45E+05
CO_2	2.62E+07	5.35E+05	2.68E+07
Globally			
CO	2.29E+07	4.20E+05	2.33E+07
PM	3.70E+05	4.20E+03	3.74E+05
NOx	4.21E+07	3.36E+04	4.24E+07
HC	6.07E+06	6.07E+04	6.13E+07
CH_4	5.96E+06	6.36E+03	5.96E+06
CO_2	3.49E+08	7.18E+06	3.56E+08

Synthetic diesel fuels are premium fuel products compared to petroleum fuels. These fuels have been demonstrated to improve diesel fuel economy by an average of 1.5% for 1995–2016 diesel vehicles as well as significantly reducing HC, PM, CO, and NOx when used as a 20 vol% blend with petroleum diesel. The Greyrock synthetic fuels have higher cetane content than petroleum fuels (about 75 vs. 45), no sulfur and aromatics, and better fuel lubricity, and they can be stored for much longer periods without degradation than petroleum-based fuels. This improved lubricity results in increased durability, efficiency, and lifetime of light-duty and heavy-duty diesel engines. In addition, the high cetane value of the synthetic fuel improves engine performance and reduces emissions.

Conclusions

This study establishes that the direct production of liquid synthetic fuels from associated flare gas at the wellhead can significantly reduce air emissions of GHGs and criteria pollutants in the US and globally. The synthetic fuels, produced from flare gas, are premium products that improve engine performance, increase engine lifetime, and decrease emissions.

A 20 vol% of the synthetic fuel blended with petroleum diesel significantly reduces non-GHG air pollutant emissions: HC (-28%), PM (-18%), CO (-24%), and NOx (-5.5%) from 1996 to 2015 diesel vehicles compared to petroleum diesel. Criteria pollutant emission reductions for this 20 vol% blend was used in the LCA models, since this was found to be an optimum blend level for improving vehicle performance and reducing emissions.

The direct conversion of associated flare gas–to–"drop-in" synthetic diesel fuels globally could reduce emissions of CO_2 and CH_4 by up to 356 and 59.6 million metric tons/year, respectively, resulting in the reduction of greenhouse gases (GHGs) by about 113.3 and 92.2% (20 year global warming potential) and 73.8 and 50.7% (100 year global warming potential) when compared to petroleum-derived gasoline fuels, respectively. Likewise, diesel criteria emissions could be reduced globally by up to 23.3, 0.0374, 42.4, and 6.13 million metric tons/year globally for CO, particulates, NOx, and hydrocarbons, respectively. The potential economic benefit of this approach is that up to 5.30 and 71.1 billion liters of synthetic fuels could be produced each year in the US and globally, respectively, from associated gas.

The direct conversion of flare gas to "drop-in" fuels at the oil wellhead results in the production of an economically valuable product from the associated gas resource that is currently wasted. The LCA results presented in this study can serve as a baseline for future comparison and as a basis for comparing

this process to other flare gas-to-fuel conversion technologies. The potential economic benefit of this approach is that up to 5.30 and 71.1 billion liters of premium synthetic fuels could be produced each year from associated gas which is currently wasted in the US and globally, respectively.

Since diesel/electric hybrids have an average fuel economy of 26.9 km/L, the advantage of producing premium, synthetic fuels from associated flare gas, and using these fuels in the hybrids will be much greater than using the fuels in standard diesel engines that average 16.6 km/L.

The results from this study can serve as a baseline for future comparison and as a basis for comparing this process to other associated flare gas conversion technologies at the wellhead. In this regard, the Argonne Laboratory GREET model has been well suited for this modeling effort and is recommended for future modeling efforts [87].

Since natural gas is a relatively clean fuel, compared to other fossil fuels, the results of this WTW-LCA study can be used in conjunction with other natural gas life cycle studies to help quantify its potential environmental, health, and ecological benefits [88–94].

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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